Synthesis and analysis of nitro compounds under zeolite catalysis.

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Synthesis and Analysis of Nitro Compounds under Zeolite Catalysis

This thesis is submitted for the degree of

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By

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DECLARATION

This work has not previously been accepted in substance for any degree and is not being concurrently submitted in candidature for any degree.

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SUMMARY

The purpose of this study was to develop a new clean method for aromatic nitration using a heterogeneous inorganic solid catalyst.

The thesis consists of four chapters. Chapter one presents an introduction to the types of heterogeneous catalyst with some details for the most important catalysts.

An electrophilic aromatic substitution is introduced in Chapter 2. Some of the latest examples of aromatic nitration using different type of nitrating reagents are discussed in this chapter.

Chapter 3 deals with the nitration of halogenobenzenes using dinitrogen tetroxide, a zeolite and oxygen in a solvent system. Zeolites Hß (Si/Al = 12.5) and Y (Si/Al = 30) were found to be the most efficients catalyst for the *para*-selective nitration of halogenobenzenes when dinitrogen tetroxide was used as the nitrating reagent over zeolite Hß in 1,2-dichloroethane. This system represents a low energy (0 °C), and potentially a clean synthesis of halonitrobenzenes using an easily recycled solvent and catalyst system.

Chapter 4 shows the nitration of aromatic compounds using dinitrogen tetroxide, a zeolite, and air in the absence of a solvent system. This system has more advantages than the previous one. Zeolite Hß (Si/Al = 12.5) was found to be the most efficient catalyst for the *para*-selective nitration of halogenobenzenes and benzene when dinitrogen tetroxide was used as nitrating reagent under 200 psi air pressure at room temperature.

CONTENTS

CHAPTER (1)

Heterogeneous Catalysts

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Heterogeneous Catalysts

1.0 Introduction

Traditionally, large amounts of reagents such as acids, bases, stoichiometric oxidant compounds and metal compounds have been used for chemical reactions in industrial processes. When these reagents are used, the yield of products is often low. In addition, the isomer products which are formed exhibit a low degree of regioselectivity. The reagents also produce toxic waste materials. These waste materials require special disposal conditions that can be both expensive and time-consuming.

To help counteract the deleterious aspects associated with the use of traditional reagents, chemists have developed heterogeneous catalysts to use in place of traditional reagents.[1] Supported reagents have also been developed recently. Some of the benefits of using these new catalysts include their high level of activity and stability and their ability to synthesize products cleanly.[2,3] There are two main types of catalyst, homogeneous, in which the catalyst and the reactants are in the same phase, and heterogeneous, in which the catalyst and the reactants are in separate phases. Heterogeneous catalysts have been used in a wide range of organic reactions because of the many advantages associated with their use.[4] For example, when heterogeneous catalysts are used, the selectivity and yield of specific reaction products often increases. Many catalysts are highly stable, have a high surface area

upon which the reaction can occur, are simple to use, show strong acidity, and can be used more than once.

One particular type of catalyst that has recently been used successfully is the class of inorganic solid materials known as zeolites. Zeolites such as β, Y and ZSM-5, can be used as solid catalysts in chemical reactions.

Because of the success of zeolites in driving organic reactions, they have become interesting subjects for research projects at the University of Wales in Swansea.[5] In fact, the current project examines the role of zeolites in the generation of regioselective nitration products.

1.1 Inorganic solid catalysts

There are several disadvantages associated with the use of traditional catalysts in chemical reactions. For example, in reactions where mineral or Lewis acids are used, large amounts of the catalysts are often required. At the same time, although the amount of catalyst used is high, the yield of the desired product is often low. In addition, the use of these acids can lead to corrosion problems and the generation of large volumes of reagents that cannot be reused. In the current environmentally conscious climate, these disadvantages are increasingly unacceptable.[6]

In contrast, the use of inorganic solid catalysts alleviates many of the environmental difficulties associated with the use of traditional catalysts. For example, Lewis or mineral acid catalysts such as $AlCl_3$ or H_2SO_4 could be replaced by H-zeolites. Replacing a lithium dialkylamide base by potassium fluoride (KF) or sodium hydroxide (NaOH) by γ-Al_2O_3 or by a polymeric equivalent would result in

the reduction of waste products produced during the reactions, thus reducing the level of environmental pollution.

1.2 Solid supports

Aluminas, silicas, clays and zeolites are inorganic substrates, that are used as supports or catalysts in organic synthetic reactions.[7] Often they exhibit an acidic or basic effect, which may be important if the rate of a reaction is to improve. In addition, zeolite catalysts exhibit a strong ability to direct regioselectivity for electrophilic aromatic substitution reactions, such as nitration. The structures and properties of each of these materials are discussed in the following sections.

1.2.1 Aluminas

There are many advantages in using aluminas or aluminium oxides in chemical reactions. They are stable even at high temperature. They are inexpensive, easy to handle and offer a wide range of pore size structures with reasonable physical strengths. Because of these characteristics, aluminas are good support materials for catalysts.

Aluminas, *i.e.* aluminium oxides, are solid, amorphous materials that do not have a regular pore or cage structure. The Al^{3+} cation occupies the central position in an octahedron and is bound to O^{2-} anions and OH^- groups. Gibbsite is an example of such a support and its structure is presented in Figure 1.1.

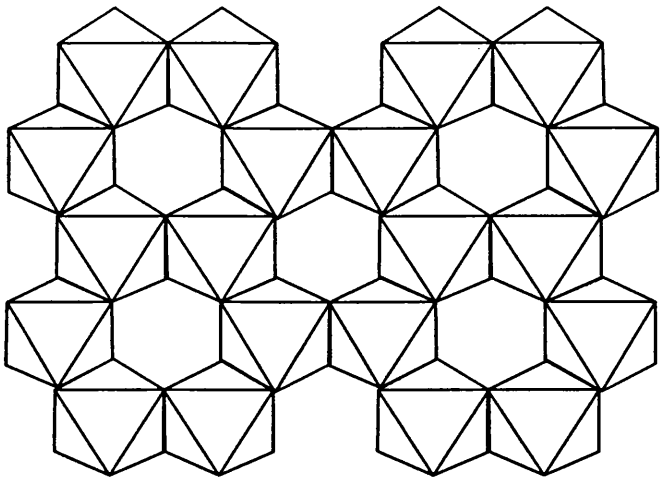


Figure 1.1. Structure of Gibbsite [$Al(OH)_3$]

Aluminas can work as acidic or basic catalysts. Whether the catalyst is acidic or basic depends on the temperature and the level of hydration of the alumina. For example, γ-Al_2O_3 is a member of the group known as transition aluminas. The decomposition sequence for the conversion of aluminum hydroxides to transition aluminas and α-Al_2O_3 is presented in Figure 1.2.[8] When aluminum trihydroxide $Al(OH)_3$ (Gibbsite) is heated to a high temperature (1100 °C) it will decompose via a variety of other forms, eventually to produce α-Al_2O_3. Generally, when a solid is heated in air, it will decompose to an oxide containing a micropore system and a surface area of hundreds of square meters per gram. However, as shown in Figure 1.2, increasing the temperature to 1100°C causes further transformation of the solid, resulting in changes to the structure of the pores, causing loss of most of the internal surface area, and giving a hard and stable crystalline material.

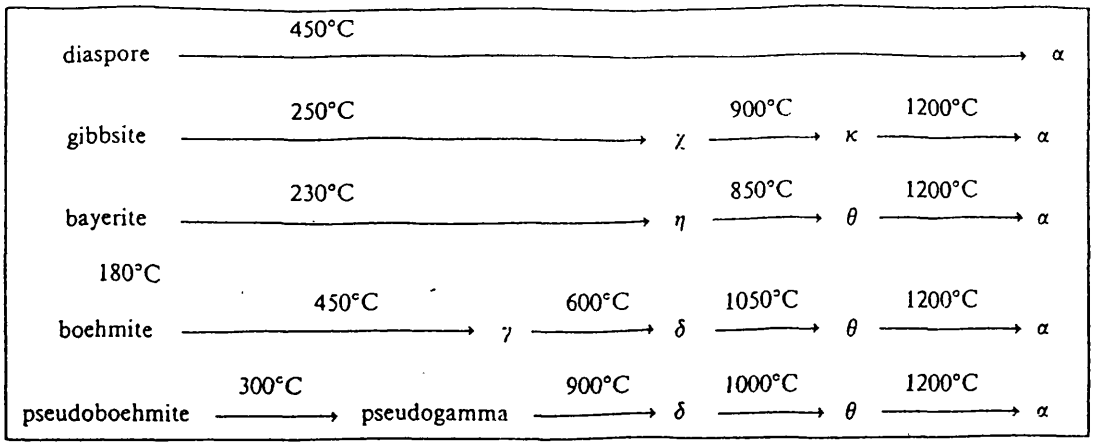


Figure 1.2. Decomposition Sequence for Conversion of Aluminum Hydroxides to Produce Transition Aluminas and α-Al_2O_3.[8]

In general, aluminas have a low surface area, although the exact surface area for a given alumina will vary depending on the density and type of the alumina solid. The amount of surface area is also related to the amount of water found in the alumina. Water is often found in the pores and channels of alumina compounds. Rapidly increasing the temperature of alumina solids evaporates the water in the pores of the alumina matrix, causing the channels of the matrix to solidify, resulting in an increase of the surface area of the alumina. Therefore, temperature has a strong effect on the surface area that is found in an alumina. The two most common types of alumina prepared by heating alumina compounds are α-Al_2O_3 and γ-Al_2O_3. γ-Al_2O_3 is formed when the alumina is treated with moderate heat, and it has been used as a solid support for different promoters, such as potassium fluoride.[9-11] It has a large

surface area. By contrast, α-Al_2O_3 is a dense solid with a low surface area and is of little use as a catalyst or support.

As shown in Figure 1.3, the method of preparation of aluminas and how they are treated has a strong effect on their ability to act as acids or bases. Aluminas are the primary compounds from which superbase materials are prepared. For example, when alumina is treated with sodium hydroxide or potassium nitrate and sodium at 280-350 °C under nitrogen gas the alumina acts as a superbase (H_more than 37).[12,13]

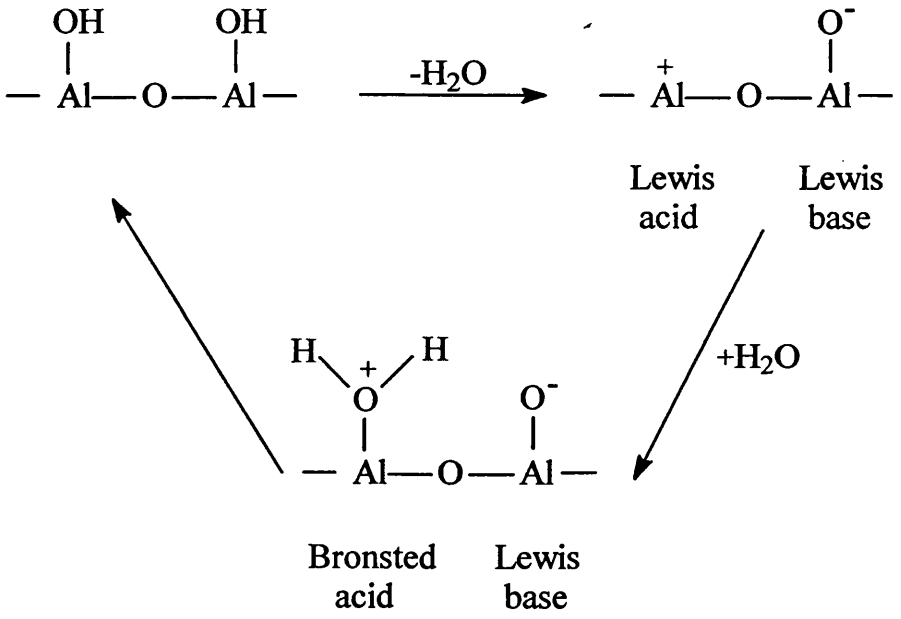


Figure 1.3. Acid and Base Sites on Alumina

1.2.2 Silica

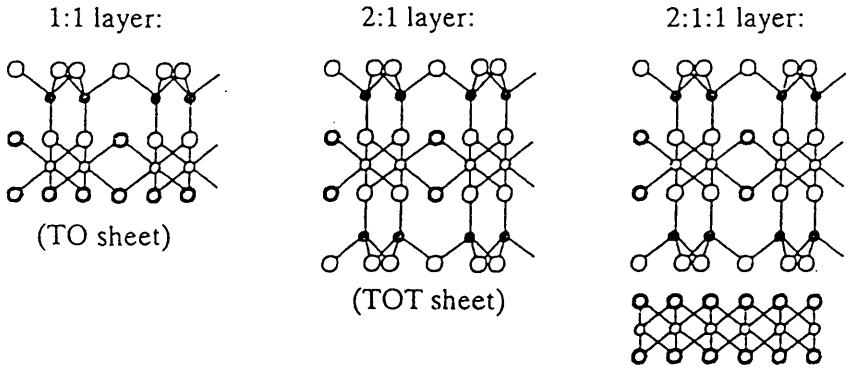
Silica or silicon dioxide (SiO_2) has Si^{4+} at the centre of a tetrahedron, with four O^{2-} groups at the apices. The tetrahedral arrangement produces a stable network of bonds through strong siloxane links. There are two general types of silica, high

density and low density silica. High density silica has a low surface area and low porosity. In contrast, low density silica has a large surface area and is more often used as a catalyst or support in organic synthetic chemistry. In fact, low density silica also has a large number of silanol (Si-OH) units and therefore it exerts a weakly acidic effect.[14-18]

1.2.3 Clays

Clays are composed of alumina and silica combinations and incorporate spaces in which cations reside. The structures of clays involve parallel sheets of tetrahedral and/or octahedral Si or Al atoms linked to each other by sharing oxygen atoms. Often the central cations are replaced by others, such as Mg^{2+}. The arrangement of these within the lattice structure of the clays, determines the type of clay obtained. There are four major groups of clays, which are termed 1:1, 2:1, 2:1:1 and 2:1 inverted ribbon (see Figure 1.4).[14-17]

Clays have been used in large numbers of organic syntheses because they possess Brønsted and Lewis acid sites, exhibit adsorption, have a large cation-exchange capacity and large surface areas, possess highly stable structures and are inexpensive.



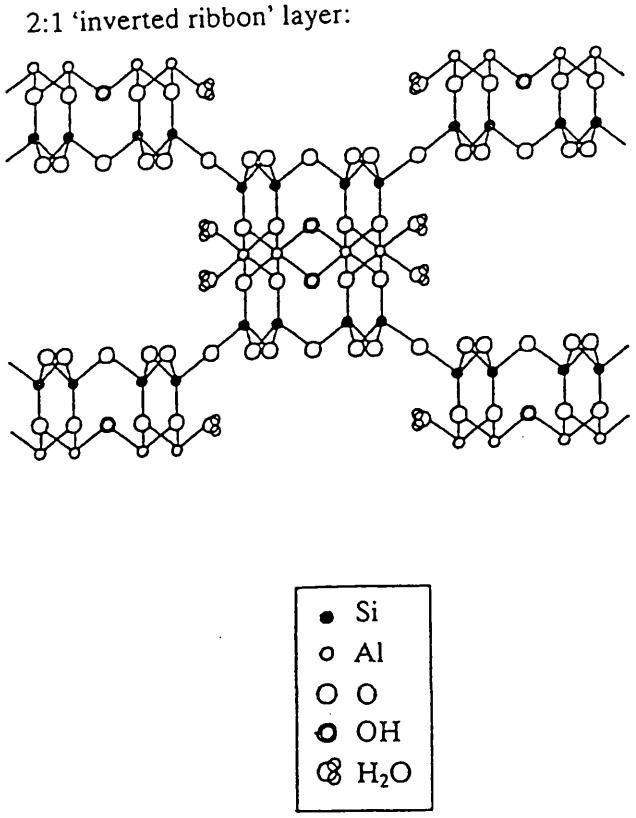


Figure 1.4. Structures of Clays

1.2.4 Zeolites

The term zeolite was introduced by A. F. Cronsted in 1756.[19] It is derived from the Greek language, and it means "boiling stone". Zeolites are classified according to their polyhedral structures.[20] Aluminosilicate units (Al-O-Si) are the foundations of the crystal structures of zeolites, which are characterized by having a matrix of pores and channels and large surface area.

There are different types of zeolites which vary in the sizes of their channels and pores. These differences produce changes in the three-dimensional structure of the zeolite, resulting in differences in the shapes, sizes, tortuosity and interconnectivity of the channels and pores of the zeolite crystals.

Water and cations occupy spaces in the pores and cages of the zeolites, and they impart special characteristics to the zeolite. The characteristics imparted to the zeolite by the cation can vary depending on the type, charge, size, concentration and the location of the cations. In addition, zeolites can be impregnated with metals, non-framework oxides and intercalated organic compounds that can also change the zeolite by providing additional phases and/or surface areas for reactivity.[21]

There are several terms associated with zeolites that are derived from the characteristics imparted by the presence or absence of water and/or cations. When zeolites contain water in their pores and surfaces, they are known as hydrated. Alternatively, dehydration of zeolites occurs when zeolites release water by heating. Zeolites can also possess a cation exchange capacity which is defined as the concentration of cations available for exchange with cations present in external

solutions. Lastly, the channels and pores of zeolites can take molecules into them.[22] This is known as intercalation.

1.2.4.1 Zeolite structures

The main structural units of zeolites are $[SiO_4]$ and $[AlO_4]^-$ tetrahedra, which are joined to each other by shared oxygen atoms to form a three-dimensional network. These tetrahedral shapes create three-dimensional frameworks that produce pores and channels for the zeolites. Zeolite structures are drawn by representing the joining of tetrahedral Si^{4+} or Al^{3+} cations by lines ignoring oxide anions between them.

Each of the $[SiO_4]$ and $[AlO_4]^-$ tetrahedra is called a primary unit used to build up the structure of the zeolite. Secondary building units (SBUs) form when the primary tetrahedral units link to each other by cation-oxygen-cation bonds. SBUs can be single ring, double ring, or complex ring structures. Single ring systems can link to form a double ring system. Single ring systems can also be modified by the addition of branches or bridges to form complex structures. Structures of the major SBUs are shown in Figure 1.5.

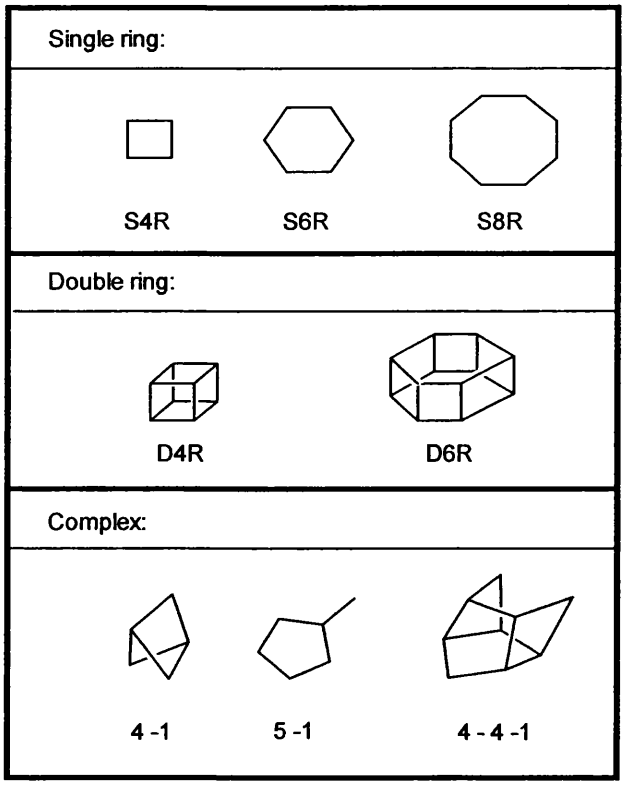


Figure 1.5. Structures of Secondary Building Units (SBUs)

Polyhedral cages and channels can be formed when the secondary building units link to each other. There are different types of polyhedral cages with different shapes because they are formed from different SBUs. Hexahedron and octahedron cage structures are considered simple polyhedral cages, which are D4R (double four ring) and D6R (double six ring) SBUs, respectively. However, the polyhedral cages can become more complicated structures when more tetrahedra are connected to each other, as in Figure 1.6. Table 1.1 shows some examples of polyhedra that can be found in the structures of various types of zeolites.

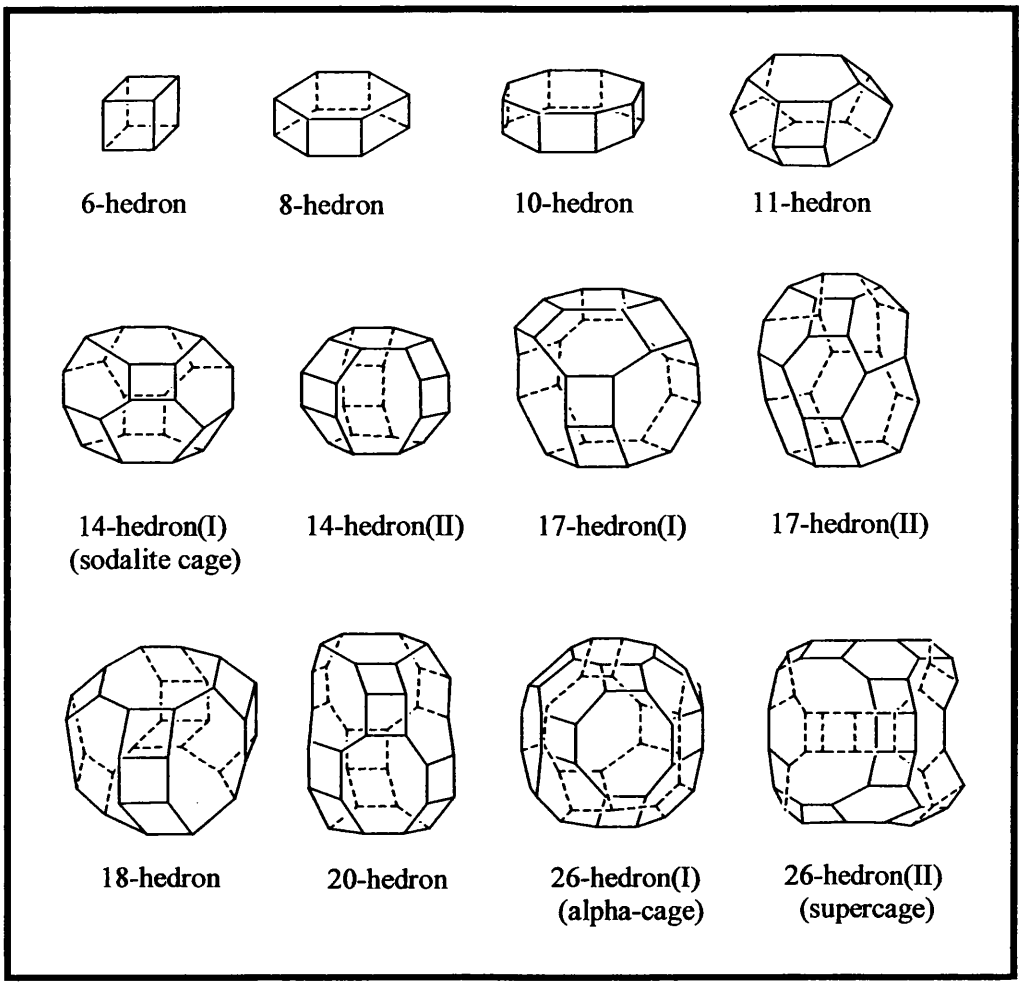


Figure 1.6. Structures of Some Polyhedral Cages

In general, zeolite structures are built up when polyhedra connect to each other by sharing their faces and channels to form crystalline three-dimensional (3D) frameworks containing pores. An aperture is located in the center of each face of the polyhedral structure. These apertures lead through to channels located in the centres of the polyhedra.

Table 1.1. Examples of Polyhedra in the Structures of Zeolites

Polyhedron	**n-Hedra**	**Type of Zeolite**
Cube	6	A
Hexagonal prism	6	Y, X
ß-Cage	14 (I)	A, Y, X
23-Hedron	23	erionite
α -Cage	26 (I)	A
Super-cage	26 (II)	Y, X

The way in which zeolites are classified is dependent on their cage and pore structures. Zeolites are grouped together with respect to their polyhedral structures and pore sizes. There are small pore zeolites, medium pore zeolites, and large pore zeolites. In the study to be reported in this thesis, zeolites having different pore sizes, namely ZSM-5, Mordenite, and β zeolites were used. More examples of zeolite classification are given in the following sections.

The diameter of the pore entrance in a zeolite plays an important role in the ability of a zeolite to contribute to a reaction taking place between reactant compounds. For example, substrate molecules, *i.e.* organic compounds, need to have a smaller molecular diameter than the pore diameter of the zeolite being used in the reaction if they are to enter the pores of the zeolite and access the interior of the zeolite crystal.

How the pore size influences the ability of a zeolite to catalyze a reaction can be illustrated by looking at various types of zeolites. In 3-T (three tetrahedron) ring zeolites, no significant apertures are present, resulting in the inability of organic compounds to be absorbed into the interior. Like the 3-T ring, a 4-T ring can be planar, but it has a large enough diameter that a small aperture can be formed. In a 5-T ring, the aperture is large at 1.5 Å but it is still too small for most organic molecules to enter. In the 6-T ring, the diameter of the aperture is 2.2 Å. The 8-T ring can have an oval shape which has a size of about 2.6 x 5.2Å or a circular shape of about 3.8 Å diameter. A 12-T ring creates a large aluminosilicate zeolite pore, and it can form planar or non-planar rings. When planar, the diameter of the aperture is about 7.6 Å. When non-planar, the diameter of the aperture is smaller, about 6.4 Å. The non-planar shape is also found in 18-T rings, which have a diameter of about 11Å.

1.2.5 Small pore zeolites

1.2.5.1 Zeolite A

Zeolite A has an 8-T ring aperture (4.1Å), which is referred to as a small pore diameter. Because of the small pore diameter, only small molecules such as water or straight chain alkanes access the interior of the zeolite crystal. Zeolite A is often used as the primary solid catalyst for drying solvents. Figure 1.7 shows the structure of zeolite A and the 8-T ring aperture. Its empirical formula is $Na_{12}[Al_{12}Si_{12}O_{48}].27H_2O$.[14] It has sodalite cages linked through face sharing cubes or hexahedra, and the void space makes a pore system of 26-hedra(I) (α-cages). By

face-sharing through 8-T rings and then linking to each other a series of α-cages is formed, as shown in Figure 1.7.

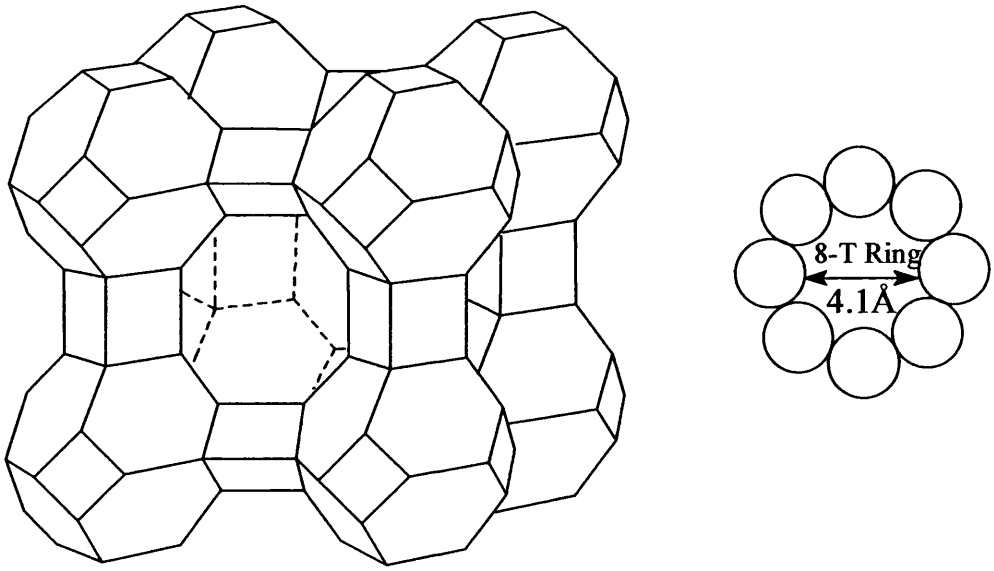


Figure 1.7. Structure of Zeolite A and 8-T Ring Aperture

The nature of the associated cation influences the pore size of zeolite A. Therefore, the classification for zeolite A is also dependent upon the identity of the cation (M^{n+}) present in the zeolite. Potassium, sodium and calcium are common cations in zeolite A. Zeolite $K^{+}A$ has a diameter of 3 Å, which is the smallest channel diameter of all of the types of zeolite A. It is often referred to as 3A molecular sieve. When zeolite A contains the sodium cation it has a channel diameter of about 4 Å and is known as 4A molecular sieve. If zeolite A contains calcium ions it has a channel diameter of 5 Å and is known as 5A molecular sieve.

1.2.6 Medium pore zeolites

1.2.6.1 Zeolite ZSM-5

Zeolite ZSM-5 (Zeolite Socony Mobil-number 5 or MFI zeolite) is an example of a medium pore zeolite. The pentasil class of zeolites, to which ZSM-5 belongs, is formed from 5-1 SUBs as shown in Figures 1.5 and 1.6. The SBUs have 10-T ring apertures as shown in Figure 1.8.

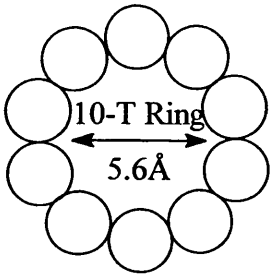


Figure 1.8. Structure of 10-T Ring Aperture

This formation leads to an oval pore shape with width 5.5 x 5.6 Å, as shown in Figure 1.9. Analysis of the three dimensional structure of this zeolite (shown in Figure 1.10a) shows that the zeolite crystal contains two types of channels, straight channels with a diameter of 5.3 x 5.6Å and sinusoidal ones with a diameter of 5.1 x 5.5Å. The sinusoidal channels are located in planes normal to the axes of the straight channels. This is represented as a set of straight, parallel pores (5.1 x 5.6Å) intersected by a set of zigzag pores (Figure 1.10b). The empirical formula is $Na_n[Si_{26-n}Al_nO_{192}].16H_2O$, where $n \leq 8$.

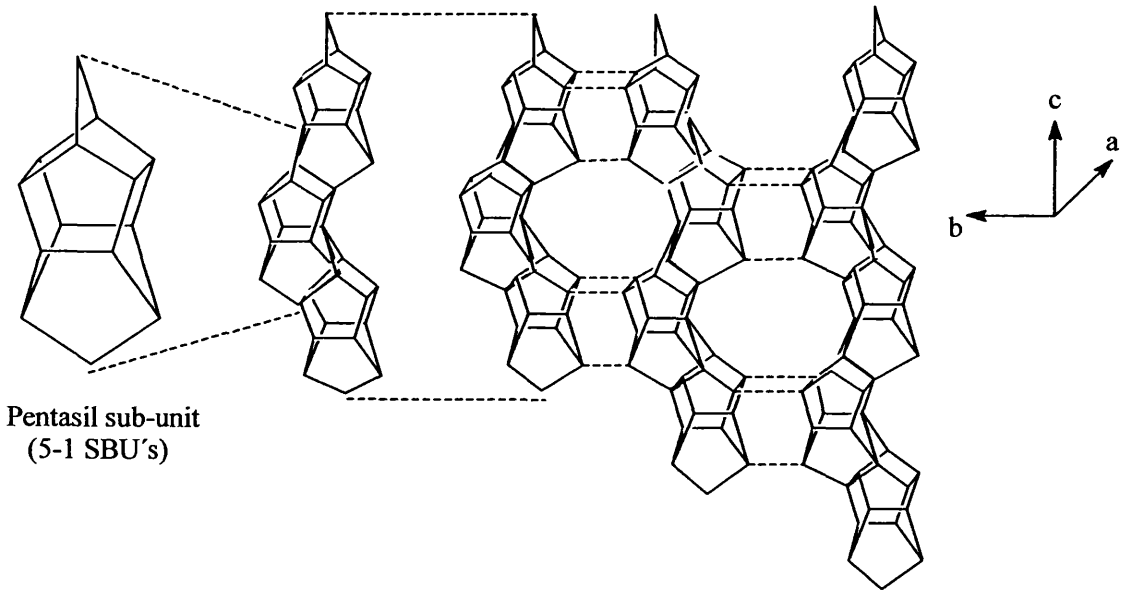
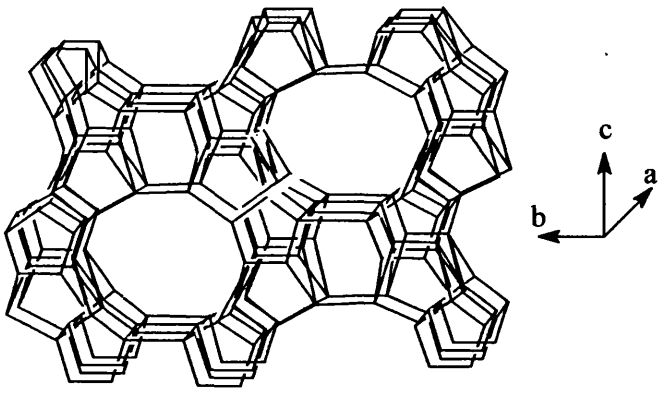
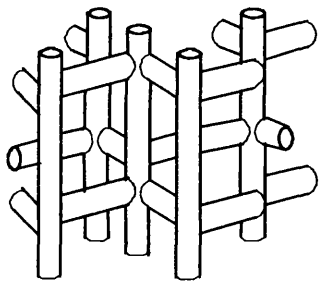


Figure 1.9. Structure of ZSM-5 Zeolite





a) Stacking structure of ZSM-5

b) Schematic representation of the intracrystalline pore structure of ZSM-5

Figure 1.10. 3D Structure of ZSM-5

1.2.7 Large pore zeolites

Three large pore zeolites were used in the current research project and were used to support and develop a new method for organic synthesis. The three catalysts which were used were zeolite β, zeolite Y and mordenite. The structures of these are described in the following section.

1.2.7.1 Zeolites X and Y

Both zeolite X and zeolite Y have a large pore size. These two zeolites have the structure of faujasite (FAU) which is shown in Figure 1.11.

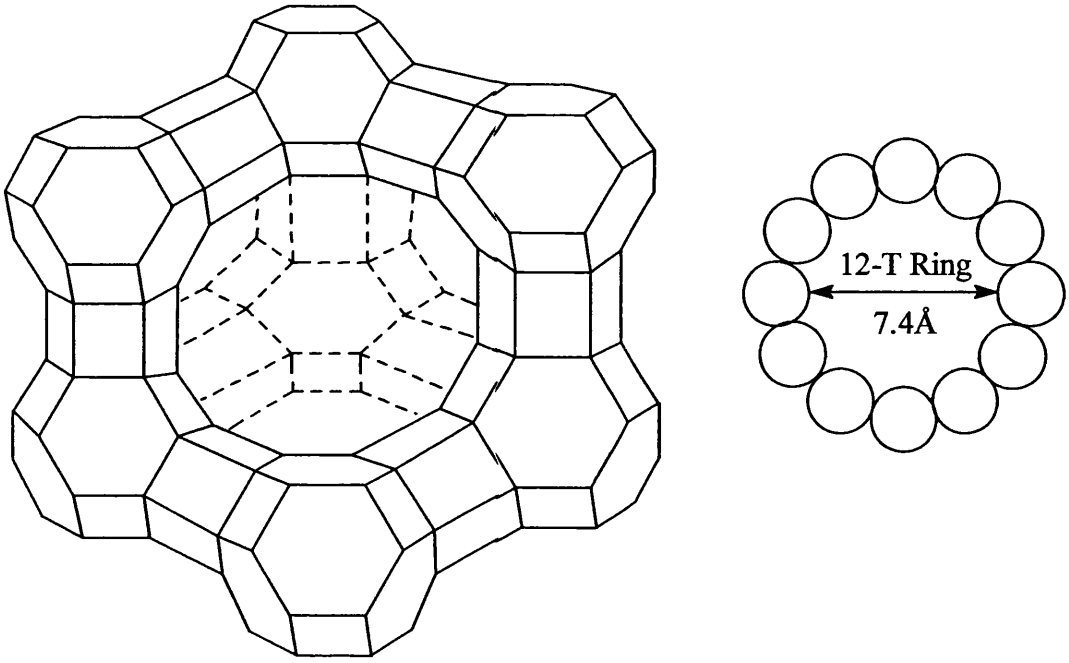


Figure 1.11. Structure of Faujasite (FAU) for Zeolites X and Y and 12-T Ring Aperture

The difference between these two zeolites is the ratio of silicon and aluminium (Si/Al). Zeolite X contains a lower amount of silicon with a Si/Al ratio of 1 to 1.5. Zeolite Y contains a ratio of silicon to aluminium that is higher than 1.5.

Because of the higher amount of aluminium found in zeolite X, its proton-exchanged form contains a higher number of acidic sites than that of zeolite Y. Both X and Y zeolites have 12-T ring apertures and the same three-dimensional pore structures. Both can be exchanged with a variety of different cations. For example, a typical empirical formula for sodium form zeolite Y would be $Na_{58}[Al_{58}Si_{134}O_{348}].24H_2O$.[14]

Both zeolites X and Y are synthesised as the sodium form. They consist of sodalite cages, linked by hexagonal prisms. The 6-T ring forms a three-dimensional system of pores which are found in the sodalite cages. Outside the sodalite cages there is a second, larger three-dimensional system of pores, which is formed in the void around the smaller channels. These large systems are called super-cages (26-hedra (II)) and are linked through 12-T ring apertures which are about 7.4Å in diameter.

1.2.7.2 Mordenite

Mordenite also contains 12-T rings and has a high content of silica. However, in contrast to zeolites X and Y, mordenite contains a one-dimensional system of channels. A typical empirical formula is $Na_8[Al_8Si_{40}O_{96}].24H_2O$.[14] The mordenite structure is formed from 5-1 SUBs linked by chains to form channels with 8-T rings,

which have dimensions about 2.6 x 5.7Å and 12-T rings, which have dimensions about 6.5 x 7.0Å. Figure 1.12 shows the mordenite structure.

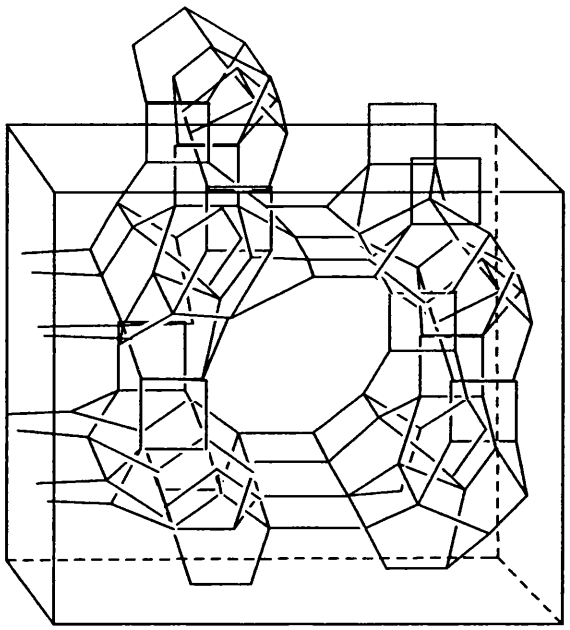


Figure 1.12. Structure of Mordenite

1.2.7.3 Zeolite β

Zeolite beta (β) was first introduced as an inorganic solid catalyst by Wadlinger in 1967.[23] This type of zeolite has a large pore size and a complex structure. It has a three-dimensional pore system with 12-T ring straight channels. It also has two pore diameters, one of 7.0 x 6.4Å and another of 5.5 x 5.5Å. The pores are present in a 2:1 ratio to each other.[24,25] The straight 12-T ring channels go in the a and b directions. The third 12-T ring channel, which is more tortuous, goes parallel to the c direction (Figure 1.13).

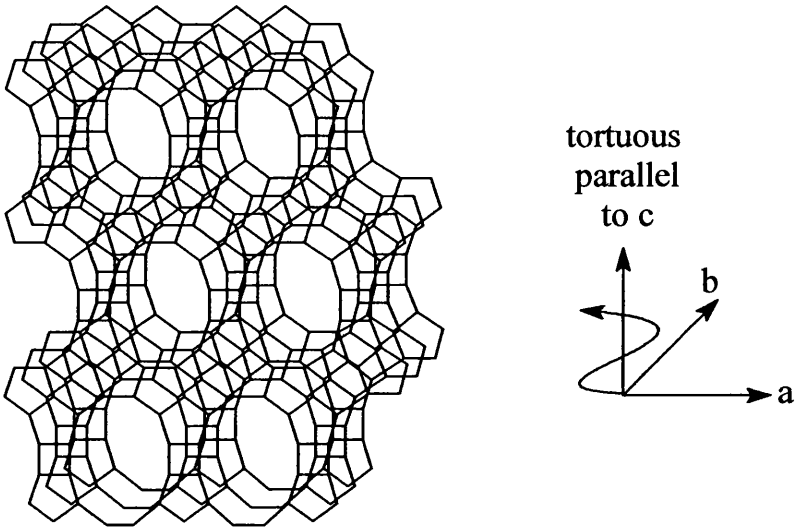


Figure 1.13. Structure of Zeolite β

There are two polymorphs of zeolite β, called A and B (Figure 1.14).[26] Polymorph A has an ABAB repeating structure and polymorph B has an ABCABC repeating structure.

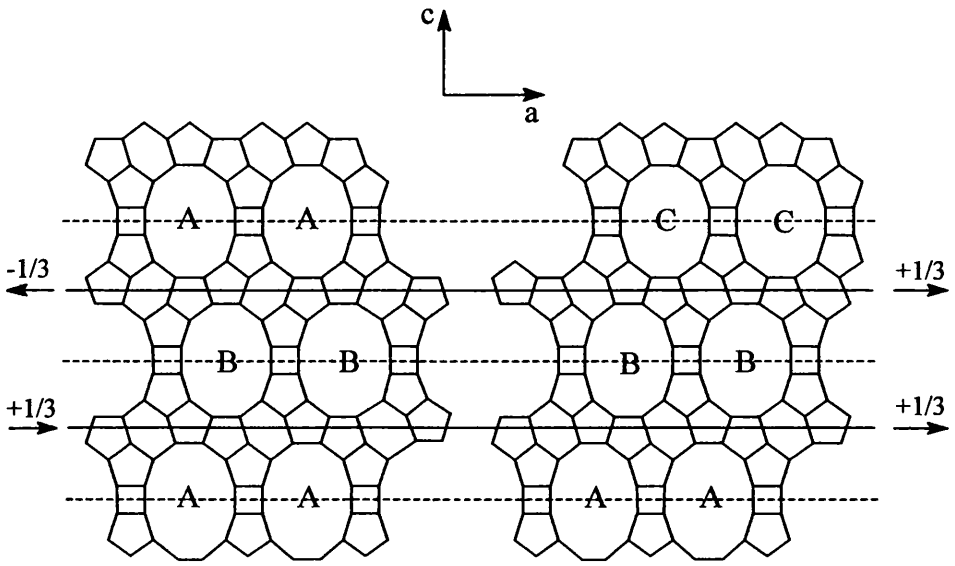


Figure 1.13. Structure of Polymorphs for Zeolite β

1.3 Composition of zeolites

The composition of zeolites covers a wide range. Even zeolites which have the same pore structure can vary in their Si/Al ratio, framework isomorphous substitution, cation exchange, intercalation and impregnation. As an example, the Si/Al ratio in zeolite ZSM-5 is 10-100, which is high compared to the typical range for most zeolites (1-5). On the other hand, the lowest Si/Al ratio possible is 1, according to Lowenstein's rule.[27] Lowenstein's rule says there can be no Al-O-Al tetrahedron linkages in the frameworks of zeolites. For example, in zeolite X the range of Si/Al ratios is 1-1.5, and in zeolite Y it is always greater than 1.5.

1.4 Cation exchange in zeolites

When the framework of zeolites contains just SiO_4 tetrahedra (as in silicalite), there are no exchangeable cations. However, when isomorphous substitution, of SiO_4 tetrahedra with AlO_4^- tetrahedra occurs, this leads to an anionic framework. Therefore, cations are required to balance the charges. The size of zeolite apertures has an important effect on the process of cation exchange (Equation 1.1). The cation can easily enter into the pores when the zeolite has a convenient aperture size. For example, solvated or hydrated cations can easily enter into the pores of zeolites that have a 8-T ring aperture or higher. In zeolites with 6-T ring apertures, cations can enter the internal pore system if they are unsolvated. In the anionic framework of zeolites, the migration of solvated cations is faster than that of unsolvated cations.

In the polyhedral cages of small pore zeolites, cations can be exchanged slowly if there is a convenient solvent. In zeolites with 6-ring apertures, higher

temperatures or longer reflux times are required for cation exchange processes, and the extent of exchange is generally less than for zeolites with 8-ring apertures. For complete cation exchange it is important to use a fresh cation solution and repeat the process of exchange several times, because cation exchange is a reversible reaction. Cation solution concentration, zeolite:solution cation ratio and zeolite nature can all influence the position of the equilibrium.

$$M_x\text{-Zeolite(s)} + M_y^+(aq) \rightleftharpoons M_y\text{-Zeolite(s)} + M_x^+(aq) \qquad (1.1)$$

1.5 Acidity of zeolites

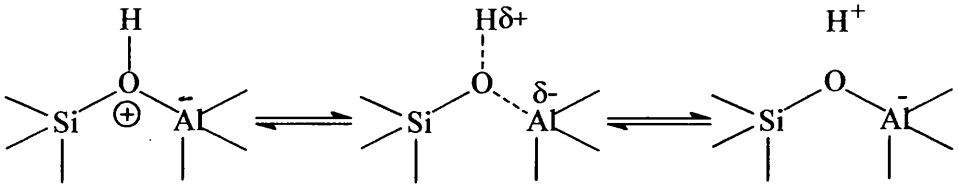
A large number of organic reactions uses zeolites as solid acid catalysts. Active Brønsted sites (acid sites) in zeolites can be increased by cation exchange using ammonium ions and then calcination at over 450 °C (Equations 1.2 and 1.3).[14,28]

$$Na^+\text{-Zeolite(s)} + NH_4^+(aq) \longrightarrow NH_4^+\text{-Zeolite(s)} + Na^+(aq) \qquad (1.2)$$

$$NH_4^+\text{-Zeolite(s)} \xrightarrow{>450\ ^\circ C} H^+\text{-Zeolite(s)} + NH_3(g) \qquad (1.3)$$

Ammonium cations are incorporated into the zeolite pores, and then when the temperature is raised to over 450 °C, the ammonium zeolite (NH_4^+–zeolite) produces

H^+–zeolite by loss of NH_3. The proton H^+, which becomes attached to an oxygen atom in the aluminosilicate network, makes the zeolite more acidic (Figure 1.14).



Brønsted acid site

Figure 1.14. Brønsted Acidity in Zeolite Structures

On the other hand, the calcination process also removes water molecules from the zeolite pores and surfaces, which leads to formation of Lewis acid sites. Water molecules are produced by removal of a proton from one hydroxyl group together with another hydroxyl group attached to a nearby silicon atom. After removal of the water, the aluminum centres become electron pair acceptors (Lewis acid sites), see Figure 1.15.

Calcination of zeolites leads to removal of two Brønsted acid sites and forms one Lewis acid site. The Lewis acid sites are oxygen deficient, unstable and lead to dealumination, which leads to non-framework alumina with Lewis acidity.[14]

There have been attempts to understand the concept of zeolite acidity.[31] As mentioned before in the section on zeolites X and Y, the lower Si/Al ratio in zeolite X and the higher Si/Al ratio in zeolite Y lead to differences in the number of acid sites in zeolites X and Y.

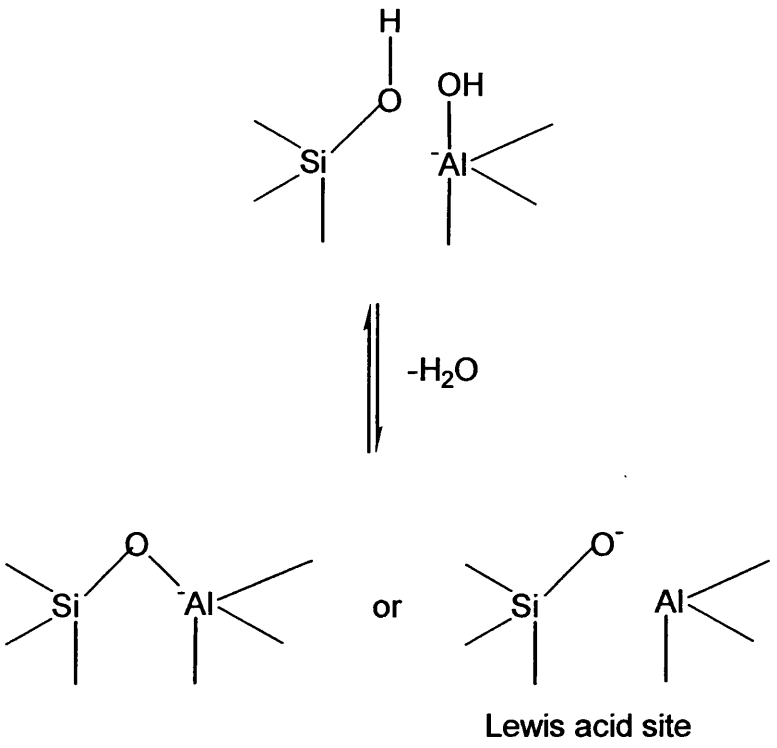


Figure 1.15. Lewis Acidity in the Zeolite Structure

The number of acid sites in zeolite X is higher than in zeolite Y, but the acid strength of individual sites is greater in zeolite Y. Understanding the structures of zeolites X and Y helps to explain the difference in acidity between them. Each AlO_4^- tetrahedron has four SiO_4 tetrahedra as neighbours, and the next nearest neighbour could be an AlO_4^- or SiO_4 tetrahedron, which is attached to the SiO_4 tetrahedron. When the amount of aluminium isomorphously substituted in the zeolite is lower (as in zeolite X) the strength of the acid site will be higher because it has fewer AlO_4^- tetrahedra in the vicinity. Therefore, increasing the Si/Al ratio increases the acid strength of the zeolites, though lowering the number of such sites.

1.6 Calcination

Heating zeolites at high temperature in air is called calcination. Even water or organic molecules, possibly resulting from the synthesis of the zeolite, can be removed by calcination. Furthermore, under high temperature (>400 °C), dehydroxylation occurs, converting Brønsted acid sites into Lewis acid centres. Under normal atmospheric conditions (room temperature) zeolites can absorb water again to reverse the process. However, keeping zeolites at high temperature for a long time can bring about irreversible changes to the structure of the zeolite crystals.

1.7 Dealumination

The process of removing aluminium from a zeolite framework is called dealumination. The process is carried out in order to increase the acid strength of individual sites and the hydrothermal stability of the zeolite structure by increasing the Si/Al ratio. It also causes a decrease in the capacity of the zeolite for cation-exchange. Dealumination can be brought about by chemical treatment, for example with acids, or by calcination. A common method is to treat the zeolite with silicon tetrachloride, which can effect replacement of Al by Si groups within the framework.[14]

1.8 Zeolite absorption

Zeolites have the capacity to absorb relatively large quantities of appropriate compounds into their pores and channels. This capacity is increased if water in the pores is first removed by heating. In general, molecules that have the same or smaller

size than the pore size can go easily through zeolite channels and cages. That means, zeolites can selectively adsorb some molecules from a mixture depending on the size of the molecules in the mixture. This is termed molecular sieving or shape-selectivity.

The chemical properties of the absorbed species and the zeolite have a strong effect on the absorption process. The type of cation-exchange and the number of Al sites of the zeolite can influence the electrostatic effect within the channels and cages of the zeolites.[29,30] Figure 1.16 shows an example of a localized non-framework cation in a zeolite. Polar molecules can be attracted to such a charged centre in the zeolite, resulting in fast and strong absorption.

The Si/Al ratio also has a strong effect on the absorption property. When the ratio is high the density of the electrostatic effect will be low, and that decreases the affinity between the zeolite and the polar molecules. For example, water is adsorbed strongly into zeolites with a low Si/Al ratio.[22,14] By contrast, zeolites with high Si/Al ratio are said to be hydrophobic.

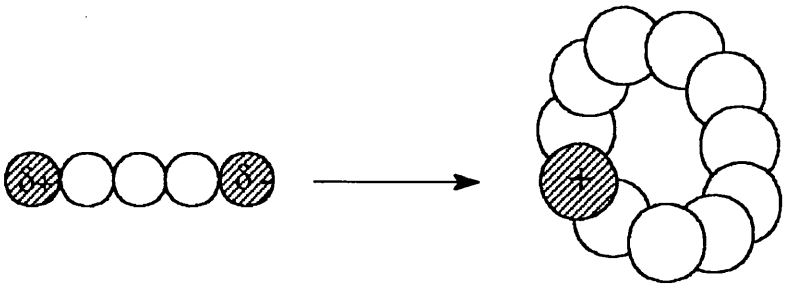


Figure 1.16. Attraction Between Polar Molecules and Charged Centre in a Zeolite

1.9 Zeolite selectivity

Zeolite selectivity depends on the connectivity, size and shape of the pore networks. When the size of reactant molecules is smaller than the pore dimensions, such molecules will pass easily through the pore network, whereas larger molecules will not pass through. This selectivity property can be helpful for separating specific isomers selectively from mixtures.[32] It can also help in directing reactions towards a particular product. [33] For example, in the chlorination of toluene over faujasite X, which was used as a solid catalyst, it was possible to increase the *para*-chlorotoluene yield substantially (Figure 1.17).[34]

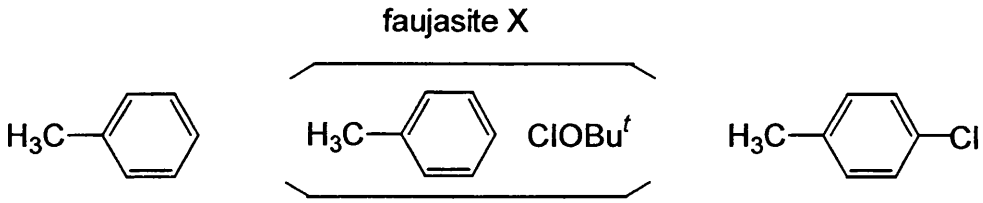


Figure 1.12. Selective *para*-Chlorination over Faujasite X

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CHAPTER (2)

Aromatic Nitration

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2.0 Introduction

Reacting aromatic compounds with a nitrating reagent results in their nitration, *i.e.* the introduction of a nitro group onto a carbon, oxygen, or nitrogen atom.[1] The introduction of a nitro group onto an oxygen atom produces a nitrate, while introduction of a nitro group onto a nitrogen atom produces a nitramine. Introduction of a nitro group onto a carbon atom of the aromatic compound is more common and gives nitroaromatic compounds. In 1825, Faraday discovered benzene. In addition, he may have been the first scientist to attempt to nitrate a benzene molecule to produce nitrobenzene.[2] In 1834, Mitscherlich was successful in nitrating benzene using fuming nitric acid as the nitrating reagent. Aromatic nitration using nitric acid and sulfuric acid (also known as mixed acids Figure 2.1) was introduced by Mansfield in 1847 for use in industry.[1] In this application, sulfuric acid was used as an inorganic catalyst, which functioned to remove the water produced during the course of the reaction, which would otherwise dilute the nitric acid concentration.[3]

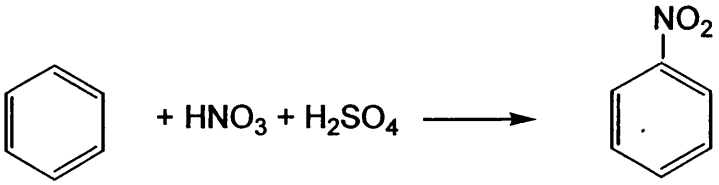


Figure 2.1. Nitration of Benzene with Mixed Acids

In the 19th century, chemists became more interested in aromatic nitration for many reasons. For one, aromatic nitration reactions were easily accomplished. In addition, by modifying the nitration conditions, the degree of nitration of the aromatic compound could be changed. For example, by modifying the nature of the nitrating reagent and the conditions under which nitration occurs, the degree of mono- and di-nitration of the reaction can be controlled. Additionally, the products of the nitration reaction and their isomers have high melting and boiling points. As an added advantage, there are reasonable differences in the melting and boiling points of the primary nitration product isomers, thus allowing for the quantitative analysis of the isomeric products. These reactions usually produce good to excellent yields of aromatic nitration products, and, these products can be converted into many derivative compounds.[4]

Another aspect of interest lies in the actual mechanism of the aromatic nitration reaction. Although some aspects of the mechanism are based on the nature of the electrophile used in the reaction, there are other aspects of the mechanism that remain to be explored. By enhancing our understanding of the mechanism of aromatic nitration, we may be able to develop new methods of aromatic nitration that will, in turn, support green chemistry.

2.1 Nitrating reagent systems

Nitrating reagent systems are used in aromatic nitration reactions. There are many different nitrating systems, and it is not appropriate to discuss each of them in depth. Only the most well-known and frequently used nitrating reagent systems will

be discussed: nitric acid alone, nitric acid/sulfuric acid, nitric acid/organic solvents, nitric acid/acetic anhydride, alkyl nitrates, and nitrogen oxides.

2.1.1 Nitric acid

Pure nitric acid can be used in aromatic nitration reactions, and many studies have evaluated the rate and the mechanism of the aromatic nitration reaction when nitric acid is used. Studies using conductrimetric, cryoscopic, and Raman spectroscopy methods indicate that, when nitric acid is used for aromatic nitration, the concentrations of nitronium and nitrate ions during the reaction are the same. This equality reduces the possible formation of nitric acidium ion, the formation of which is dependent on Equation 2.1.[5]

$$2HNO_3 \rightleftharpoons H_2NO_3^+ + NO_3^- \qquad (2.1)$$

When low concentrations of nitric acid are used, the amount of nitronium ion is reduced as shown in Equation 2.2.

$$NO_2^+ + NO_3^- + H_2O \rightleftharpoons 2HNO_3 \qquad (2.2)$$

However, the kinetic order of the reaction remains unchanged, which would indicate that the small amounts of nitronium ions present during the reaction are reacting with water. In order for the kinetic order to be altered, water must remove

nitric acidium ions rather than nitronium ions. This implies that nitric acidium ions are the true precursors of nitronium ions as shown in Equations 2.3 through 2.5.

$$2HNO_3 \underset{}{\overset{K1}{\rightleftharpoons}} H_2NO_3^+ + NO_3^- \quad (2.3)$$

$$HNO_3 + H_3O^+ \overset{K2}{\rightleftharpoons} H_2NO_3^+ + H_2O \quad (2.4)$$

$$H_2NO_3^+ \overset{K3}{\rightleftharpoons} H_2O + NO_2^+ \quad (2.5)$$

However, the rate for aromatic nitration reaction using nitric acid as nitrating reagent was interesting subject for many researchers.[4] The rate at which nitration occurs in the presence of concentrated nitric acid is considerably altered by the presence of strong acids or nitrate anions, neither of which alter the concentration of nitric acid significantly.

2.1.1.1 Aromatic nitration using zeolite β and the nitric acid system

An interesting study in which zeolite β was used as a catalyst along with nitric acid as the nitrating reagent in the nitration of toluene and selected halogenobenzenes and alkylbenzenes was reported by Choudary *et al.*[6] Toluene was nitrated using different clays or zeolites with nitric acid. Then, the catalyst that yielded the highest amount of *para*-nitrotoluene in the experiments was used as the catalyst in a series of experiments in which several halogenobenzenes and alkylbenzenes were nitrated.

The reaction times, concentrations of nitric acid solution, and the results are presented in Table 2.1.

Table 2.1. Yield and Isomer Distributions of Nitrotoluenes Produced by Nitrations Using Nitric Acid Over Various Clays and Zeolites as Solid Phase Inorganic Catalysts, According to Choudary *et al.*[6]

Catalyst Type	**Time (h)**	**HNO_3 (%)**	**Yield (%)**	**Isomer Distributions (%)**		
				ortho	***meta***	***para***
Fe^{3+} Mont.	22.8	90	89	53	3	44
K-10 Mont.	9.1	60	53	45	3	52
Hß (Si/Al = 22)	10.6	60	68	30	3	67
Hß (Si/Al = 27)	6.8	60	40	41	4	55
HZSM-5	5.6	60	32	49	7	44
H-Mord.	6.0	60	35	56	6	38
HY	5.4	60	32	54	7	39

As shown in Table 2.1, the yield of nitrotoluene varied from 32% when HZSM-5 or zeolite HY as used as the catalyst to 89% when iron montmorillonite, a clay catalyst, was used. The proportion of *para*-nitrotoluene varied from 38% when mordenite was used to 67% when zeolite Hβ (Si/Al = 22) was used.

The overall yield when zeolite Hβ (Si/Al = 22) was used as the catalyst was lower than that obtained when iron montmorillonite was used as the catalyst, but the reaction was conducted for a much shorter time and starting with more dilute nitric acid.

However, the proportion of *para*-nitrotoluene was higher when zeolite Hβ (Si/Al = 22) was the catalyst employed in the reaction mixture, indicating, that, in this

procedure, zeolite Hβ (Si/Al = 22) was the best catalyst to use for *para*-selective nitration of toluene. It is interesting to note that two different types of catalysts, a clay and a zeolite, produced very similar results in terms of the selectivity of *para*-nitrotoluene formation, although the overall yields of nitrotoluene were very different. Iron montmorillonite gave the highest yield of nitrotoluene, 89%.

Use of zeolite Hβ (Si/Al = 22) produced the next highest yield of nitrotoluene, 68%. However, the selectivity of the reactions for the *para*-isomer was almost the same. A couple of different hypotheses were proposed to explain why the use of zeolite Hβ (Si/Al = 22) led to the highest selectivity for *para*-nitrotoluene.

The differences between the reactivity of the clay and the zeolite can be explained by analyzing their structural matrices. These two catalysts differ from one another in terms of their structure, and these differences play a vital role in shaping the types of reactions they can catalyse. Iron montmorillonite, a clay, has a two-dimensional sheet-like structure, while the zeolites have a three-dimensional, interconnected structure. The two-dimensional structure of the clay leads to easier accessibility of the active sites and thereby an increased overall yield of nitrotoluenes, but the selectivity of the reaction is limited. In contrast, the three-dimensional structure of the zeolites allows for an increase in the selectivity of the reaction if the pore dimensions are right, but a lower accessibility of the active sites, which could lead to a decrease in the overall yield.

However, two zeolites Hβ were used in this series of experiments, and their use produced very different overall yields and *para*-selectivities. Zeolite Hβ (Si/Al = 22) had an overall yield of 68%, and the proportion of *para*-nitrotoluene was 67%. In

contrast, when zeolite Hβ (Si/Al = 27) was used, the overall yield of nitrotoluene was 40% and the proportion of *para*-nitrotoluene was 55%. The use of the zeolite with the lower silicon to aluminium ratio produced a little over twice as much *para*-nitrotoluene as the zeolite with the higher silicon to aluminium ratio. It may be possible to explain these results by looking at how the ratio of silicon to aluminium may affect how the nitration reaction occurs.

The two aspects of the zeolite that are affected by changes in the silicon to aluminium ratio are the number of Brønsted acid sites within the zeolite matrix and the pore size of the matrix. As the amount of aluminium within the zeolite decreases, two things happen. First, the number of Brønsted acid sites decreases. Since these reactions are, at least in part, dependent on the acidity of the nitrating environment, decreasing the number of reactive sites within the matrix leads to a decrease in the rate of nitration, which may in turn lead to a lower yield of nitration products produced during the course of the reaction. And, from the results of these experiments, it is clear that the reactivity of the zeolite Hβ does decrease as the silicon to aluminium ratio is increased. When zeolite Hβ (Si/Al = 27) is used, the overall yield of nitrotoluene is only 40%. In contrast, when the zeolite Hβ (Si/Al = 22) is used, the overall yield of nitrotoluene is 68%.

The second effect of dealumination of the zeolite is related to the pore size of the zeolite. A lower Si/Al ratio was probably achieved by dealumination of a sample of zeolite that initially had a higher ratio. As aluminium is removed from the matrix, the size of the pores within the matrix increases, leading to a loss in selectivity of the

reaction. Thus, the yield of *para*-nitrotoluene is less when the zeolite Hβ (Si/Al = 27) is used than when zeolite Hβ (Si/Al = 22) is used (Table 2.2).

In the light of these results, zeolite Hβ (Si/Al = 22) was used as the catalyst in a series of reactions in which different halogenobenzenes and alkylbenzenes were nitrated.[6] The reaction times, concentrations of nitric acid solution, and the results are presented in Table 2.2.

Table 2.2. Yields and Isomer Distributions of Products Produced Using Zeolite Hβ (Si/Al = 22) as the Catalyst for the Nitration of Halogenobenzenes and Alkylbenzenes with Nitric Acid, According to Choudary *et al.*[6]

Substrate Type	**Time (h)**	**HNO_3 (%)**	**Yield (%)**	**Isomer Distributions(%)**		
				ortho	***meta***	***para***
Chlorobenzene	12.0	60	51	10	-	90
Bromobenzene	15.8	70	52	18	-	82
Iodobenzene	19.8	70	52	28	-	72
Propylbenzene	12.8	70	51	19	-	81
Methoxybenzene	11.4	70	49	25	-	75

The overall yields of nitrotoluenes were modest regardless of which compound was used as the substrate. However, the selectivity of this reaction for the *para*-isomer is very high. The best *para*-selectivities were obtained when chlorobenzene was nitrated, and the lowest *para*-selectivities were obtained when iodobenzene was the substrate, in line with the normal trends for electrophilic substitution of halogenobenzenes.

There are two primary influences involved in producing the results obtained in these experiments. First, the electron-withdrawing and electron-donating characteristics of each of the substituents on the benzene ring influence how the benzene ring is nitrated. For example, as the electron-withdrawing capacity of the substituent increases, the positive charge on the two carbon atoms located at the *ortho* positions also increases, and *vice versa*. Since the nitronium ion, NO_2^+, is a positively charged species, it is repelled by the positive charge on the carbons at the *ortho* position. The second characteristic that is involved in determining where the nitronium group will bond on the benzene ring is the directive capability of the substituent group. Some substituents are *meta* directors, while others are *ortho/para* directors. In these experiments, all of the substituents are *ortho/para* directors.

In the case of the halogenobenzenes, as the electronegativity of the substituent increases, so does the level of *para*-nitrated product. Of the three halogen substituents, chlorine has the highest level of electronegative, and the yield of *para*-chlorobenzene is higher than the yield of *para*-nitrated product obtained when bromine and iodine, both of which have lower electronegativity values than chlorine, are the substituents on the benzene ring. The yield of *para*-nitrated product is also greater than the yield of *ortho*-nitrated product when propylbenzene is the substrate, and, again, this can be related to the electronegativity and directive characteristics of the substituent group. Generally, alkyl groups are weak electron-donating groups and direct electrophilic reactions to the *ortho* and *para* positions of the aromatic ring. In these cases, bonding of the nitronium ion at the *meta* position is unlikely, not only

because these substituents are *ortho/para* directors, but also because of the limitations imposed by the pore size of the zeolite catalyst.

From these experiments, it is apparent that the use of zeolite Hβ (Si/Al = 22) in the nitration of toluene, halogenobenzenes, and alkylbenzenes is a very effective method for producing *para*-nitrated aromatic products. Although the yields are modest, the *para*-selectivity is high for each of the substrates that were examined. However, this system is not without its disadvantages. First, the reaction is very sensitive to the presence of water. If water is present in the system, the active sites on the catalyst cannot be regenerated. The need continually to remove water from the system increases the difficulties and level of complexity within the experimental setup. Second, large amounts of substrate need to be used in the experiment, and the yields relative to the amount of substrate used are low. The substrate that has not been nitrated can be recovered from the reaction mixture and reused in subsequent experiments, but that takes time and money. Alternatively, the unreacted substrate can be discarded, resulting in the waste of reagents. Either way, there are expenses associated with the unreacted substrate that would not be there if the reaction produced higher yields of nitrated substrate.

2.1.1.2 Aromatic nitration using mordenite and nitric acid

Shimada *et al.* reported the nitration of chlorobenzene using mordenite as the catalyst and nitric acid as the nitrating reagent.[7] In addition to mordenite, Shimada *et al.* also reported the results obtained from experiments in which other solid catalysts were used to promote the nitration of chlorobenzene.

In Shimada's procedure, diluted sulfuric acid and catalyst were mixed and the water was evaporated at 140 °C. The dry catalyst was calcined at 200 °C for four hours, then heated at the desired temperature while nitric acid and chlorobenzene were added. The temperature to which the catalyst was heated, the percentage of nitric acid contained in the nitric acid solution that was added to the catalyst, and the amount of chlorobenzene added to the catalyst per hour varied from experiment to experiment. The length of time for which each experiment was conducted is not entirely clear, although it seems that the reaction time for each experiment was six hours. The experimental conditions and the results are presented in Table 2.3.

In these experiments, both the conversion and overall yields of nitrochlorobenzene are modest. The conversion ranges from 4.1% to 17.3% when different alumina and silica catalysts are used. No information about conversion was provided when mordenite was used as the reaction catalyst.

The *para*-selectivity of these reactions is low, with values ranging from 21% when alumina oxide (Al_2O_3) is used as the catalyst to 70% when mordenite is used as the reaction catalyst. Overall, the results of this series of experiments indicate that this method of aromatic nitration is not very effective, at least, not when chlorobenzene is used as the substrate. Nitration using this method requires large amounts of substrate, high reaction temperatures, and the use of concentrated nitric and sulfuric acids. Under these conditions, the use of large amounts of substrate, especially when considering the low percent conversion of substrate to product, low overall yields, and low degree of *para*-selectivity of the reaction, leads to the waste of large amounts

of substrate. In addition, there are safety hazards associated with the use of high reaction temperatures and the employment of concentrated acid solutions.

Table 2.3. Conversion, Yield, and Isomer Distribution when Chlorobenzene is Nitrated with Nitric Acid Over Solid Catalysts, According to Shimada *et al.*[7]

Catalyst Type	**HNO_3 (%)**	**Temp. (C°)**	**Conversion (%)**	**Proportion Converted to Product[b] (%)**	**Isomer Distributions (%)**		
					ortho	***meta***	***para***
H_2SO_4-mord.	72	185	-[a]	64	29.1	1.3	69.6
H_2SO_4-Al_2O_3	72	185	14.1	7.7	77.5	1.4	21.1
H_2SO_4 -SiO_2	62	232	7.9	2.0	71.1	2.8	26.1
$MgSO_4$ -SiO_2	62	162	4.1	0.8	31.7	1.7	66.6
$Fe_2(SO_4)_3$ -SiO_2	62	167	8.1	4.3	24.8	1.7	73.4
$Fe_2(SO_4)_3$ -SiO_2	98	170	17.3	8.0	30.5	1.3	68.2

[a]No value for conversion of substrate to product was provided for this experiment. [b]The author used the term "yield" without explanation, but it is clearly impossible for the actual yield to exceed the amount converted, so it would appear that the reported figures are probably the proportion of starting material consumed that was converted into product.

2.1.2 Nitric and sulfuric acid system

Aromatic nitration using nitric acid and sulfuric acid is called the "mixed acid" method. By adding a strong acid such as sulfuric acid to nitric acid the nitronium ion concentration is increased through protonation of the nitric acid to form nitric acidium ion, which leads to rapid dissociation of HNO_3. Simply, sulfuric acid supports the ionization of the nitric acid to the nitronium ion, which is the nitrating species. In addition to allowing the formation of the nitronium ion, the sulfuric acid binds the water formed during the course of the reaction.

In this system, the ratio of nitric acid to sulfuric acid exerts a strong effect on the mono-selectivity of the nitrated products.[8] Furthermore, the nature of both the solvent and the aromatic compound involved in the reaction can alter the concentration of nitronium ions formed.[9] For example, increasing the concentration of sulfuric acid from 58% to 65% leads to an increase in the amount of nitro compounds formed. When 58% sulfuric acid is used, the primary compound formed is mononitrotoluene. When 65% sulfuric acid is formed, the dinitrotoluene amount starts to go up. [10]

A mechanism for aromatic nitration using the nitric acid and sulfuric acid system was reported by Ingold,[11] and many of the steps were presented previously in equations 2.3 through 2.5. In the final stage, the nitrating species (NO_2^+) reacts with the substrate to give the nitro compound (Equation 2.7).

$$HNO_3 + H_2SO_4 \overset{K4}{\rightleftharpoons} H_2NO_3^+ + HSO_4^- \quad (2.6)$$

$$NO_2^+ + ArH \xrightarrow{K5} ArNO_2 + H^+ \quad (2.7)$$

Ingold noticed that nitrate ions inhibited nitration without changing the kinetic order. He then suggested that the nitrate ions did not exert their effect by consuming NO_2^+. Rather, the nitrate ions affected the concentration of the nitronium ion precursor, the nitric acidium ion. Equations (2.3), (2.4) and (2.6) show the formation of the nitric acidium ion. In the presence of an acid catalyst, Equation (2.6) supercedes step (2.3), and the presence of substantial amounts of water (as shown in Equation (2.4)) becomes important. Furthermore, Hanson reported that the nitrate ion did not deprotonate the nitric acidium ion (Equation 2.3), but instead deprotonated the acid involved in forming the nitric acidium ion.[4]

2.1.3 Nitric acid and an organic solvent system

The most popular organic solvents used in this type of nitration system are nitromethane, tetramethylene sulfone (sulfolane), tetrachloromethane, and acetic acid. When organic solvents are used for nitration using nitric acid, the solvent provides the aromatic compound with a medium in which it is soluble, which supports using milder reaction conditions to facilitate nitration, constituting the primary advantage of using this system for aromatic nitration. Furthermore, using organic solvents leads to a lower the acidity of the medium (reaction mixture) than is obtained when using only a mixture of acids, which is important for some aromatic nitration reactions.

Table 2.4 illustrates examples of nitrating systems for aromatic nitration that employ nitric acid or mixed acids in organic solvent systems. It is clear that the selectivity for *para*-nitrotoluene was increased from 34.6% to 41% by increasing the percentage of the mixed acid from 30% to 75% when the sulfone solvent was used.

This change is due to the acidity change within the reaction mixture. In contrast, increasing the percentage of acetic acid used as the solvent did not change the selectivity for *para*-nitrotoluene.[12]

Table 2.4. Nitration of Toluene by Using Nitric Acid and Mixed Acid in Different Organic Solvent Systems at 25 °C.[12]

Nitrating System	**Isomer Distribution (%)**		
	ortho	***meta***	***para***
HNO_3-CH_3NO_2	61.5	3.1	35.4
HNO_3-AcOH	56.9	2.8	40.3
HNO_3-sulfolane	61.9	3.5	34.7
HNO_3-CF_3CO_2H	61.6	2.6	35.8
30% of 1:1-Mixed acid- sulfolane	62.0	3.4	34.6
30% of 1:1-Mixed acid- AcOH	56.5	3.1	40.4
75% of 1:1-Mixed acid- sulfolane	56.3	2.6	41.0
75% of 1:1-Mixed acid- AcOH	58.1	1.9	40.0

For acetic anhydride, it should be pointed out, that acetyl nitrate ($AcONO_2$) is the nitrating reagent acting as the carrier for the NO_2^+ ion, and that is produced by reacting nitric acid with acetic anhydride (Ac_2O) (Equation 2.8).

$$Ac_2O + HNO_3 \longrightarrow AcONO_2 + AcOH \qquad (2.8)$$

The type of solvent used in aromatic nitration reactions of halogenobenezenes also affects both the yield and the *para*-selectivity of the reaction. These effects are illustrated in Table 2.5 for reactions in which chlorobenzene is nitrated using nitric acid or a mixed acid system.[13] From this table, it is clear that adding either acetic anhydride and/or carbon tetrachloride to a nitric acid or mixed acid system increases the *para*-selectivity of the reaction when chlorobenzene is nitrated. In general, when halogenobenzenes are used in reactions, the charge produced by the electron withdrawing characteristics of the halogen atom induces formation of *ortho* reaction products. Solvents of relatively low dielectric constant (AcOH) allow more interactions between this charge and the electrophile (NO_2^+), thereby decreasing *ortho* substitution.[13]

Table 2.5. Nitration of Chlorobenzene Using Nitric Acid or Mixed Acid Systems with Acetic Anhydride and/or Carbon Tetrachloride.[13]

Nitrating System	**Yield (%)**	**Isomer Distribution (%)**	
		ortho	***para***
HNO_3-AcOH	1	33	67
HNO_3-H_2SO_4	90	34.6	65.4
HNO_3-Ac_2O	8	22	78
HNO_3-Ac_2O-H_2SO_4	66	19.5	80.5
HNO_3-Ac_2O-CCl_4-H_2SO_4	-	18	82

2.1.4 Nitric acid and acetic anhydride system

Reacting acetic anhydride and nitric acid with toluene produces nitrotoluene with a high degree of *para*-selectivity.[14,15] According to A. Musson's thesis, the reaction between nitric acid and acetic anhydride has been said to take place in two steps, as shown in Equations 2.8 and 2.9.[4]

$$AcONO_2 + HNO_3 \longrightarrow AcOH + N_2O_5 \qquad (2.9)$$

Acetyl nitrate, $AcONO_2$, is produced in the first step (Equation 2.8). In the second step of the reaction, the newly formed acetyl nitrate is said to react with another molecule of nitric acid, producing dinitrogen pentoxide, N_2O_5.

Water is also formed during the nitration reaction, but the use of acetic anhydride results in the removal of water from the reaction mixture, producing acetic acid, as shown in Equation 2.10.

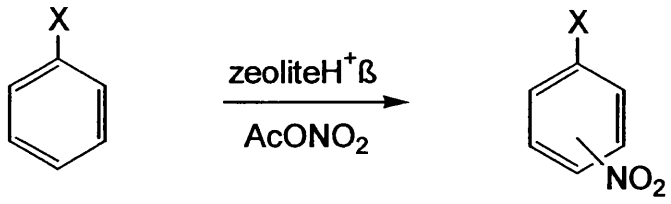
$$Ac_2O + H_2O \longrightarrow 2AcOH \qquad (2.10)$$

The removal of water from the reaction mixture when acetic anhydride is used represents the primary advantage of using this reaction system.

2.1.4.1 Aromatic nitration using zeolite Hβ catalyst and acetyl nitrate

Smith *et al.* reported an interesting method in 1998.[14] In this method, zeolite Hβ (SiO_2/Al_2O_3 = 25) was used as the catalyst and acetyl nitrate was used as the nitrating reagent.

Once the acetyl nitrate has been formed, it can react with aromatics in the presence of zeolite Hβ (SiO_2/Al_2O_3 = 25), as shown in Equation 2.11, where X represents the substituent bound to the aromatic ring.



(2.11)

As shown in Table 2.6, this nitration system produces excellent yields of nitrated aromatic compounds. In addition, the system is highly *para*-selective. However, although this system is easy to use, with short reaction times and high overall yield and regioselectivity, there are two disadvantages to using this system.

Table 2.6. Yield and Isomer Distributions Formed when Zeolite Hβ (SiO_2/Al_2O_3 = 25) and Acetyl Nitrate are Used to Effect Nitration of Various Aromatic Compounds, According to Smith *et al.*[14]

Substrate Type	**Yield (%)**	**Isomer Distributions (%)**		
		ortho	***meta***	***para***
Benzene	>99	-	-	-
Fluorobenzene	>99	6	-	94
Chlorobenzene	>99	7	-	93
Bromobenzene	>99	13	-	87
Toluene	>99	18	3	79

The first disadvantage is associated with the presence of water in the system. As in some of the other nitrating systems that have been discussed, this nitrating system is very sensitive to the presence of water. In the presence of water, acetic acid is formed as shown in Equation 2.8.

Since acetyl nitrate is the nitrating reagent in this system, the formation of acetic acid severely impairs the nitrating ability of the system.

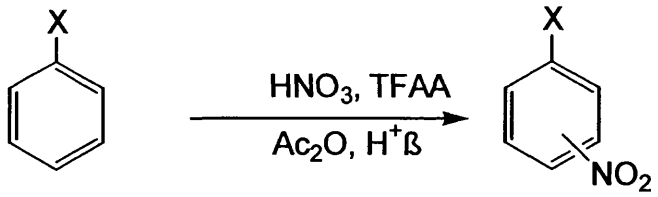
According to A. Musson, the second disadvantage is related to the reaction that forms the nitrating reagent.[4] As shown in Equation 2.8, the nitrating reagent, acetyl nitrate, is formed by reacting acetic anhydride with nitric acid. According to A. Musson, in this system, it is important that the amounts of nitric acid and acetic anhydride are used in exactly the right ratios.[4] If nitric acid is used in excess of the acetic anhydride, the acetyl nitrate produced through the reaction of nitric acid with acetic anhydride can react with the excess nitric acid, forming dinitrogen pentoxide, as shown in Equation 2.9.[4]

If this statement is correct, dinitrogen pentoxide is an extremely powerful explosive compound, and pure acetyl nitrate will also explode spontaneously at 60°C under atmospheric pressure, leading to a very serious safety hazard.[16] Therefore, this method is not ideal for large scale work.

2.1.4.2 Aromatic nitration using zeolite Hß catalyst with acetyl nitrate and trifluoroacetyl nitrate as reagents

Nitration of aromatic compounds has also been reported using zeolite Hβ (SiO_2/Al_2O_3 = 25) with acetyl nitrate and trifluoroacetyl nitrate as the nitration

reagents. This work was reported by Smith *et al.* in 2000.[15] In their work, an attempt was made to nitrate three different halogenobenzenes, nitrobenzene, benzoic acid, and cyanobenzene. The nitration reaction occurs according to Equation 2.12, where X represents the substituent on the ring (see Table 2.7).



(2.12)

As shown in Table 2.7, the yields of nitrated halogenobenzenes were excellent, greater than 97% for each of the three halogenobenzenes used in these experiments.

Table 2.7. Yields and Isomer Distributions when Zeolite Hβ (SiO_2/Al_2O_3 = 25) was Used as the Catalyst with Acetyl Nitrate and Trifluoroacetyl Nitrate as the Nitrating Reagent, According to Smith *et al.*[15]

Substrate Type	**Yield (%)**	**Isomer Distribution (%)**		
		ortho	***meta***	***para***
Fluorobenzene	>99	<1	0	99
Chlorobenzene	>99	7	<1	92
Bromobenzene	>97	11	0	89
Nitrobenzene	25	2	91	7
Benzoic Acid	74	11	79	10
Cyanobenzene	17	10	71	19

In addition, the *para*-selectivity of the reactions was also very high, with *para*-isomer proportions of 89% or higher for each of the substrates used. However, the yields and *para*-selectivities of the reactions with nitrobenzene, benzoic acid, and cyanobenzene were not as high as those obtained when the halogenobenzenes were used. The overall yields for these substrates ranged from of 17% for cyanobenzene to 74% for benzoic acid. The *para*-selectivity was low for all three of the *meta*-directing compounds. However, the proportion of the *para*-isomer in each case is higher than for traditional methods of nitration.

In general, the system produces high overall yields of nitrated halogenobenzenes, as well as products that are highly selective for the *para*-isomers. The results obtained with nitrobenzene, benzoic acid, and cyanobenzene are not as promising. Overall the method is simple to use, however, the system is sensitive to the presence of water, requires the maintenance of a low temperature throughout the experiment, and uses a concentrated nitric acid solution. These requirements increase the level of difficulty and complexity associated with the use of the system in aromatic nitration reactions.

2.1.5 Alkyl nitrates

Alkyl nitrates, R-O-NO_2, are inherently stable compounds and can be used successfully in the nitration of aromatic compounds. Although these compounds are easy to use and can alter the ratio of *ortho* to *para* reaction products, they are not usually capable of aromatic nitration when used independently of other compounds. Instead, strongly polarized compounds such as Lewis acids or sulfuric acid need to be

used in conjunction with the alkyl nitrates in order to effect nitration of aromatics.[17] For example, the results of experiments using methyl nitrate, CH_3-O-NO_2, alone in the presence of toluene indicated that toluene was not nitrated.[18] However, when boron trifluoride, BF_3, was used as the catalyst to support the reaction, toluene was nitrated according to the scheme shown in Figure 2.2.

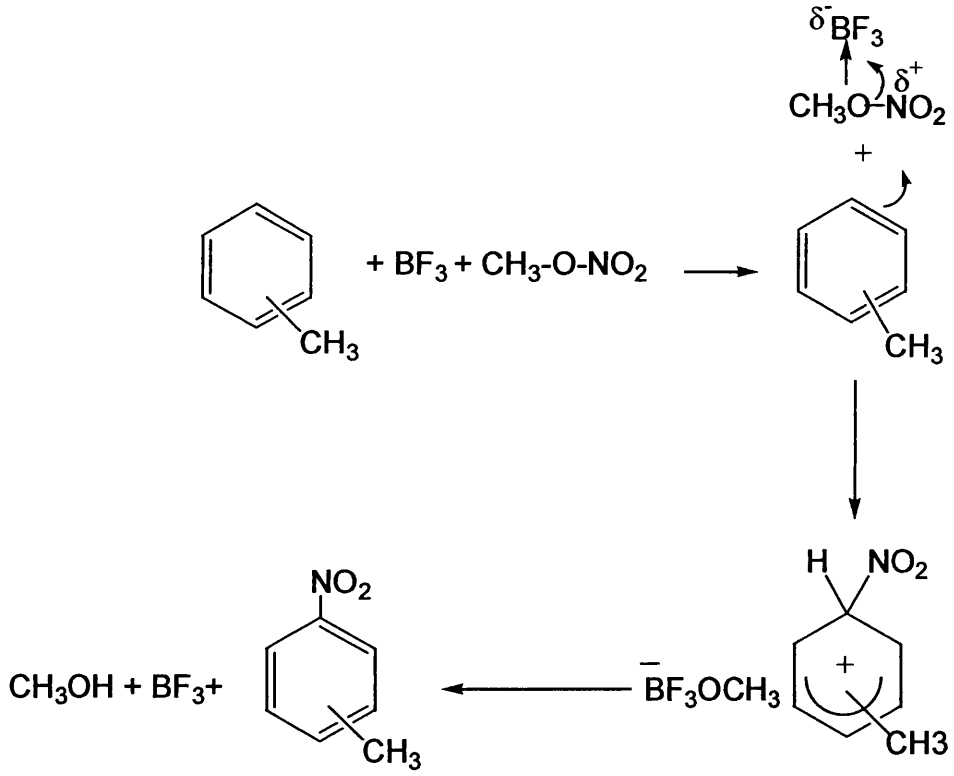


Figure 2.2. Nitration of Toluene Using Methyl Nitrate, CH_3-O-NO_2, and Boron Trifluoride

Subsequent studies using infrared spectroscopy and Raman spectroscopy of the reaction shown in Figure 2.2 indicated that nitronium ion (the typical nitrating

species) is not generated during this reaction, indicating that another nitrating species is responsible for nitrating toluene.[18]

As mentioned previously, the *para*-selectivity of aromatic nitration reactions can be altered when alkyl nitrates are used, and the percentage of *ortho*, *para*, and *meta* products produced when different aromatic compounds are reacted with methyl nitrate using boron trifluoride (BF_3) as the catalyst in nitromethane solvent is presented in Table 2.8.

Table 2.8. Comparison of *ortho*, *para*, and *meta* Selectivity of Aromatic Nitration Products Using Methyl Nitrate with Boron Trifluoride in Nitromethane Solvent.[18]

Substrate Type	**Isomer Distribution (%)**		
	ortho	***meta***	***para***
Toluene	63.9	3.4	32.7
Fluorobenzene	11.1	0.3	88.6
Chlorobenzene	31.4	1.0	67.6
Bromobenzene	33.3	1.3	65.4
Iodobenzene	41.8	1.6	56.6

2.1.6 Nitrogen oxides

Although nitrogen oxides are commonly used as nitrating reagents, not all nitrogen oxides can function in this capacity. A list of nitrogen oxides and their reactivity in nitrating reactions is presented in Table 2.9.[19]

Table 2.9. Identities and Properties of Nitrogen Oxides.[19]

Name	**Temperature (°C)**	**Color**	**Stability and Reactivity**
Nitrous oxide (N_2O)	Melting Point: -90.8 Boiling Point: -88.5	Colorless	Stable; rather unreactive
Nitric oxide (NO)	Melting Point: -163.6 Boiling Point: -151.8	Colorless	Stable; moderately reactive
Dinitrogen trioxide (N_2O_3)	Freezing Point: -100.6 Decomposition: 3.5	Dark Blue	Extensively dissociated as gas; reactive in nitration
Dinitrogen tetroxide (N_2O_4)/ Nitrogen dioxide (NO_2)	Boiling Point: 21.15 Freezing Point: -11.2	Brown Colorless	Extensively dissociated to NO_2 as gas and partly as liquid; reactive in nitration
Dinitrogen pentoxide (N_2O_5)	Melting Point: 30 Decomposition: 47	Colorless	Unstable as gas; reactive in nitration

Interestingly, individual nitrogen oxides that are not typically used as nitrating reagents due to their lack of reactivity can be used to prepare other nitrogen oxides that can be used as nitrating reagents. A good example of this is in the use of nitrous oxide, N_2O, and nitric oxide, NO. Neither of these two compounds is typically used as a nitrating reagent. However, when nitrous oxide and/or nitric oxide are reacted with oxygen, dinitrogen trioxide, N_2O_3, is formed which can be used as a nitrating reagent.[20]

The use of each of the nitrating nitrogen oxides presented in Table 2.9 is discussed in the following section.

2.1.6.1 Dinitrogen trioxide

As mentioned previously, reacting nitrous oxide and/or nitric oxide with oxygen forms the nitrating reagent, dinitrogen trioxide. The dissociation of dinitrogen trioxide at temperatures above -30 °C yields nitrosonium and nitrite ions, as shown in Equation 2.13.

$$N_2O_3 \rightleftharpoons NO^+ + NO_2^- \qquad (2.13)$$

In addition to temperature dependent dissociation, dinitrogen trioxide may also exhibit self-ionization when in the liquid phase (Equation 2.13).[19]

As is the case when alkyl nitrates are used as nitrating reagents, the use of dinitrogen trioxide does not produce the nitronium ion, NO_2^+, a strongly electrophilic ion, as the nitrating species. Rather, the active nitrating species when dinitrogen

trioxide is used is the nitrosonium ion, NO^+, which is less electrophilic than the nitronium ion. The identity of the nitrating species was determined by Raman spectroscopy when dinitrogen trioxide and sulfuric acid were reacted together. The equation for this reaction is presented in Equation 2.14.[21]

$$N_2O_3 + 3H_2SO_4 \rightleftharpoons 2NO^+ + 3HSO_4^- + H_3O^+ \qquad (2.14)$$

Nakano *et al.* have published a method for producing nitrated aromatic compounds using dinitrogen trioxide.[20] In their method, liquid dinitrogen trioxide is produced by reacting nitric oxide, NO, with oxygen at liquid nitrogen temperature. However, according to Nakano's work, because the nitrosonium ion is a less electrophilic species, the yield of nitrated aromatics is lower than when the nitronium ion is the nitrating species. For example, the nitration reaction of toluene produced 71% nitromethylbenzene and just 2% nitrotoluene, which was present as a mixture of *ortho-* and *para*-nitrotoluenes.[20] The conversion for this reaction was 82% after a 14 hour reaction time at 60 °C.[20] The low yields of various nitrated aromatic compounds are presented in Table 2.10 in which benzene, toluene, and chlorobenzene were nitrated using dinitrogen trioxide in conjunction with boron trifluoride (N_2O_3-BF_3) in an organic solvent.[22]

Table 2.10. Aromatic Nitration Using Dinitrogen Trioxide and Boron Trifluoride in the Presence or Absence of Nitroethane.[22]

Substrate	**Reaction Conditions**	**Nitrated Products**	**Yield (%)**
Benzene	Solvent: none	Nitrobenzene	5
	Temperature: 45°C		
	Reaction Time: 42 hours		
Toluene	Solvent: nitroethane	*o*-Nitrotoluene	56
	Temperature: 65°C	*p*-Nitrotoluene	1
	Reaction Time: 72 hours		
Chlorobenzene	Solvent: nitroethane	*o*-Chloronitrobenzene	12
	Temperature: 95°C	*p*-Chloronitrobenzene	50
	Reaction Time: 24 hours		

2.1.6.2 Dinitrogen tetroxide and nitrogen dioxide

Many researchers have studied the nitration of aromatic compounds using dinitrogen tetroxide and nitrogen dioxide. The role of catalysts in promoting aromatic nitration has also been studied, and Schaarschmidt was the first investigator to study the catalytic effect of aluminum chloride, $AlCl_3$, and ferric chloride, $FeCl_3$, on the nitration of aromatic compounds in the presence of dinitrogen tetroxide.[23] In 1958, another researcher, Bachman, reported the successful nitration of aromatics using a stable dinitrogen tetroxide-boron trifluoride complex, $N_2O_4BF_3$.[24] In his work, the *para*-selectivity for the nitration of chlorobenzene was 60%, a higher percentage of *para*-selectivity than is seen when the mixed acid nitrating reagent is

used to facilitate nitration. Yet another researcher, Olah reported aromatic nitration using dinitrogen tetroxide and sulfuric acid as the nitrating system. The percentage of sulfuric acid used and the yield of products are presented in Table 2.11.[23]

Table 2.11. Aromatic Nitration Using the Dinitrogen Tetroxide, N_2O_4, and Sulfuric Acid, H_2SO_4, Nitrating System.[23]

Substrate	**H_2SO_4 Concentration (%)**	**Yield (%)**
Benzene	80.2	95
Toluene	77.6	94
Chlorobenzene	84.5	95
Nitrobenzene	100.0	94

The formation of the nitronium ion, NO_2^+, when the dinitrogen tetroxide and sulfuric acid nitration system was used was confirmed using Raman spectroscopy. The results of this study indicate that the nitronium ion is formed according to Equation 2.15.

$$N_2O_4 + 3H_2SO_4 \longrightarrow NO_2^+ + NO^+ + H_3O^+ + 3HSO_4^- \quad (2.15)$$

Dinitrogen tetroxide and nitrogen dioxide exist in a mobile equilibrium with one another as shown in Equation 2.16.

$$N_2O_4 \rightleftharpoons 2NO_2 \qquad (2.16)$$

The equilibrium depends on the temperature of the system in which they are found. The dissociation of dinitrogen tetroxide to nitrogen dioxide is not well understood, and studies using mass spectrometry have been undertaken to help elucidate the process by which the dissociation occurs. However, these studies were not successful in providing information about the species involved in the dissociation process under normal conditions. Research has shown that some of the dissociation occurs when nitrogen dioxide and dinitrogen tetroxide are in the liquid phase. At the freezing point, -11.2 °C, the liquid is yellow in color and contains 0.01% NO_2. An increase in the percentage of NO_2 is seen when the temperature is increased to the mixture's boiling point, 21.15 °C. At this temperature, the percentage of NO_2 present is 0.1%, and the colour of the mixture changes to a deep reddish-brown. Increasing the temperature to 100 °C results in the movement of the system from the liquid phase to the gas phase and produces 90% NO_2 and 10% N_2O_4. The dissociation of dinitrogen tetroxide to nitrogen dioxide is complete at 140 °C, at which temperature the percentage of NO_2 is 100%.[19,25] In addition, further increases in temperature lead to the further dissociation of NO_2 to NO and oxygen. This dissociation begins when the temperature is higher than 154 °C and is complete when the temperature reaches 600 °C.

The dissociation of dinitrogen tetroxide can occur either homolytically or heterolytically. Homolytic dissociation produces nitrogen dioxide free radicals as shown in Equation 2.17.[25]

$$N_2O_4 \rightleftharpoons O_2N^{\cdot} + {}^{\cdot}NO_2 \qquad (2.17)$$

Alternatively, heterolytic dissociation produces either nitronium and nitrite ions or nitrosonium and nitrate ions as shown in Equations 2.18 and 2.19.[19,25]

$$N_2O_4 \rightleftharpoons NO_2^+ + NO_2^- \qquad (2.18)$$

$$N_2O_4 \rightleftharpoons NO^+ + NO_3^- \qquad (2.19)$$

In aromatic nitration using the dinitrogen tetroxide/nitrogen dioxide system, nitronium ion, NO_2^+, is the nitrating species and is produced when the unpaired electron located on NO_2 is lost. Hence, dissociation of dinitrogen tetroxide by heterolytic dissociation may offer an explanation of how these reactions occur when dinitrogen tetroxide is present in the liquid phase or when it is dissolved in solvents.[25] Although this does offer a plausible explanation for how the nitronium ion is produced, there is no physical evidence to support the dissociation scheme presented in Equation 2.18 when pure dinitrogen tetroxide is used.[25] However, in pure dinitrogen tetroxide there is some evidence to support dissociation according to the scheme presented in Equation 2.19.

Dinitrogen tetroxide and nitrogen dioxide can be prepared in several different ways.[19] Thermal treatment of lead nitrate, $Pb(NO_3)_2$, produces dinitrogen tetroxide

and nitrogen dioxide, as does reacting silver nitrate, $AgNO_3$, with nitrosyl chloride, NOCl. These reactions are presented in Equations 2.20 and 2.21.[25]

$$2Pb(NO_3)_2 \xrightarrow{\Delta} 2PbO + O_2 + 4NO_2 \qquad (2.20)$$

$$AgNO_3 \xrightarrow{NOCl} AgCl + N_2O_4 \qquad (2.21)$$

Even acids can be used to prepare dinitrogen tetroxide. This is accomplished by reacting nitric acid, HNO_3, with sulfur dioxide, SO_2, according to Equation 2.22.[25]

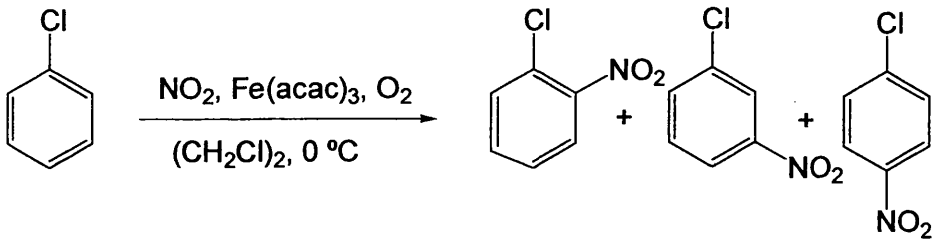
$$2HNO_3 + SO_2 \longrightarrow N_2O_4 + H_2SO_4 \qquad (2.22)$$

Aromatic compound nitration using dinitrogen tetroxide as the nitrating reagent is discussed in more detail in the following sections.

2.1.6.2.1 Aromatic nitration using the dinitrogen tetroxide-$Fe(acac)_3$-oxygen system

The use of a metal, acetylacetonate (acac) catalyst, also promotes the nitration of aromatic compounds when dinitrogen tetroxide is used as the nitrating reagent. Acac complexes of iron(III), cobalt(III), manganese(III), copper(II) and cerium(IV) have been found to promote the nitration of aromatic compounds in liquid dinitrogen tetroxide, primarily yielding mononitrated aromatic compounds.[26,27] In 1997, Suzuki reported the use of dinitrogen tetroxide as the nitrating reagent, oxygen as the

oxidation reagent, and $Fe(acac)_3$, as the inorganic catalyst for the nitration of aromatic compounds. The chemical equation for this reaction, when chlorobenzene is used as the starting compound, is shown in Equation 2.23.[28]



(2.23)

The results of this experiment, as well as the results of other experiments in which the starting compound and the reaction time were varied, are presented in Table 2.12.[28]

Table 2.12. Nitration of Aromatic Compounds Using the Dinitrogen Tetroxide $Fe(acac)_3$-Oxygen System of Nitration.[28]

Substrate Type	**Time (h)**	**Yield (%)**	**Isomer Distribution (%)**		
			ortho	***meta***	***para***
C_6H_6	24	83	-	-	-
C_6H_5-CH_3	12	80	55	2	43
C_6H_5-Cl	36	93	32	<1	68
C_6H_5-OCH_3	1	55	40	<1	60
C_6H_5-$COCH_3$	72	29	51	49	<1
C_6H_5-$NHCOCH_3$	6	33	73	<1	27

In these experiments, the overall yield of nitrated product was good when toluene was nitrated, especially when compared to the results obtained when anisole, acetophenone or acetanilide as used as the starting compound. The same was true when benzene was used as the starting compound. However, in terms of selectivity, the system yielded nitrated products with approximately the same level of selectivity for *para*-nitrotoluene as when the mixed acid (41%) system was used for the nitration of toluene.[1]

When chlorobenzene is used as the starting compound, the yield of nitrated chlorobenzene is high, 93%, and the selectivity for the formation of *para*-nitrochlorobenzene (56%) is slightly higher than when the mixed acid method is used for the nitration of chlorobenzene.[29]

Suzuki has suggested a mechanism by which the $Fe(acac)_3$ catalyst affects the nitration of aromatic compounds when the liquid dinitrogen tetroxide-oxygen system is used, and this mechanism is shown in Figure 2.3.[28]

In this mechanism, nitrogen dioxide first complexes with $Fe(acac)_3$ to form the iron complex shown in Box (A). The new complex reacts with another two molecules of nitrogen dioxide to produce the active species shown in Box (B). In the presence of an aromatic, some of this active complex oxidizes the aromatic, forming an aromatic radical cation.

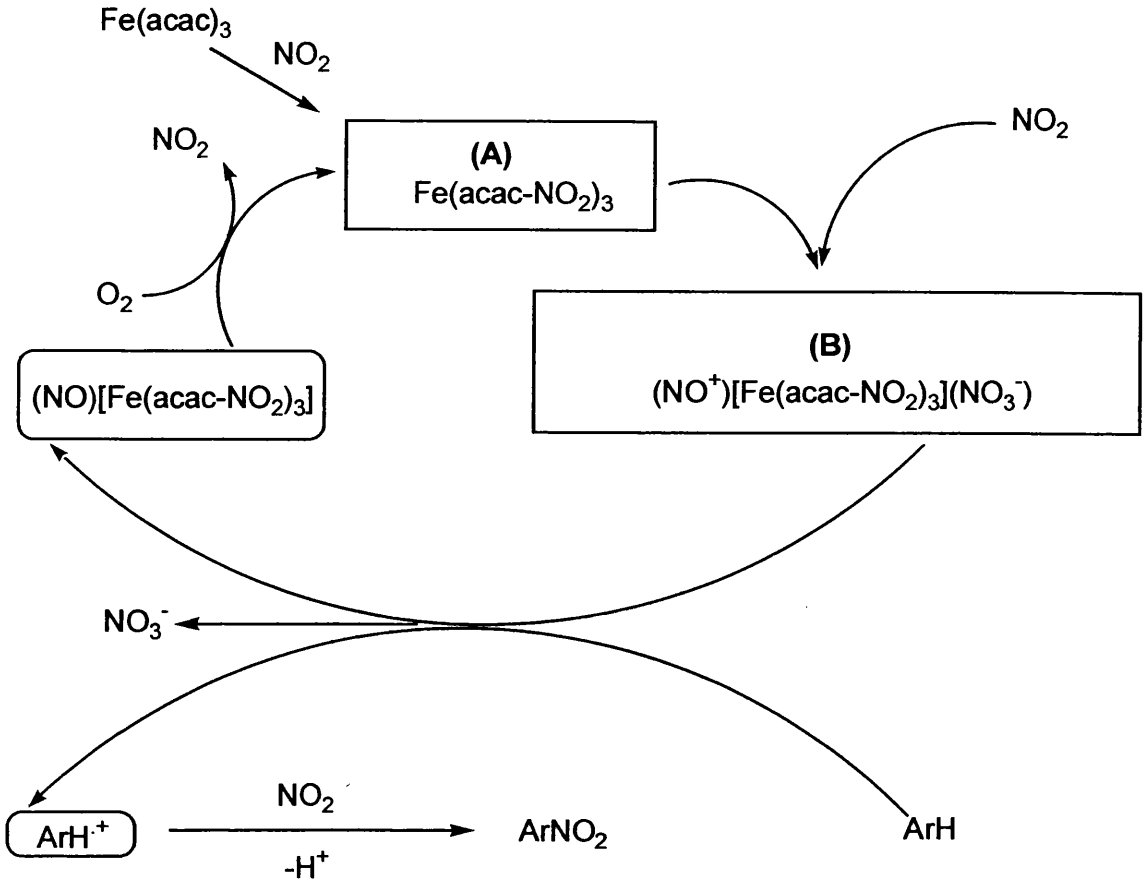


Figure 2.3. Mechanism of Aromatic Nitration Using Dinitrogen Tetroxide $Fe(acac)_3$-Oxygen System, as Proposed by Suzuki.[28]

The mononitrated aromatic compound is then produced through the addition of NO_2 and subsequent loss of a proton.

Although Suzuki's work has dealt primarily with $Fe(acac)_3$, this is not the only type of metal acetylacetonate compound that can be used to facilitate aromatic nitration. In fact, Roos *et al.* reported the nitration of benzene using the dinitrogen tetroxide-oxygen system and different types of metal acetylacetonate compounds.[27] The results of Roos' work are shown in Table 2.13.[27]

Table 2.13. Nitration of Benzene Using Different Types of Metal Acetylacetonate Complexes as Catalysts in the Dinitrogen Tetroxide-Oxygen Nitration System.[27]

Metal Acetylacetonate Complex	**Catalyst (mmol)**	**Time (min)**	**Yield (%)**
$Fe(acac)_3$	1.85	70	16.1
$Co(acac)_3$	1.98	68	15.6
$Mn(acac)_3$	2.0	58	6.6
$Cu(acac)_2$	3.8	55	6.8
$Ce(acac)_4$	1.54	44	8.1

As shown in Table 2.13, the highest yields of nitrobenzene were obtained when either $Fe(acac)_3$ or $Co(acac)_3$ as used as the inorganic catalyst under the particular experimental conditions; the yields of nitrobenzene when any of the other three catalysts as used were less than 10%. Although the yields of nitrobenzene when $Fe(acac)_3$ or $Co(acac)_3$ as employed were almost the same, they were still less than the yields achieved by Suzuki. In Suzuki's work, as shown in Table 2.12, the yield of nitrobenzene when $Fe(acac)_3$ was used as the inorganic catalyst was 83%, five times more than the yield achieved by Roos.

As indicated, there is quite a difference between the yields obtained by Roos and Suzuki when $Fe(acac)_3$ was used as the catalyst in the nitration reaction. In all probability, these differences can be linked to three different experimental parameters. The first parameter that has varied is the reaction time. In Suzuki's work, the reaction time for the nitration of benzene using $Fe(acac)_3$ was 24 hours,

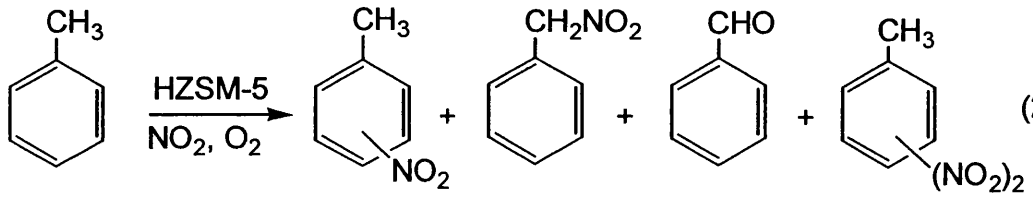
while in Roos' work, the reaction continued for only 70 minutes. Another difference was in the type of solvent used during the course of the experiment. Roos used nitromethane as the solvent, while Suzuki used 1,2-dichloroethane. The third difference was in the order in which the compounds were added to one another. In Roos' work, the dinitrogen tetroxide was oxidized by oxygen first, then added to the substrate. Following its addition to the substrate, the metal-acac catalyst was added to the mixture and the reaction was allowed to continue. In Suzuki's work, $Fe(acac)_3$ and the substrate were mixed together with the solvent, then the dinitrogen tetroxide was introduced to the system. Following the addition of dinitrogen tetroxide, the system was placed under oxygen for 24 hours.

Because there are so many differences in the way in which these two sets of experiments were performed, it is difficult to pinpoint exactly why or how these two experimenters produced significantly different results in the yield of nitrobenzene. Although it is possible that the solvent and the order in which the reactants were mixed together played a role in the overall yield of nitrated benzene achieved at the end of the reaction, the differences in the yield of nitrobenzene achieved in these different experiments are most likely related to the length of time the reactions were allowed to continue. In Suzuki's experiment, the reaction continued for 24 hours, while the reaction continued for only 70 minutes in Roos' experiment. Thus, it seems likely that, had Roos' reaction continued for a longer period of time, the yield of nitrobenzene would have been higher. However, if Roos' experiment had been continued for a comparable length of time and the yield of nitrobenzene was still low, then more insight could have been gained into how solvents and the way in which

they are combined with the other reagents in the reaction impact on the efficiency of nitration reactions.

2.1.6.2.2 Aromatic nitration using zeolite HZSM-5 and nitrogen dioxide

Use of zeolite HZSM-5 and zeolite Hβ along with nitrogen dioxide has been reported by H. Suzuki *et al.*[30] In this work, toluene and chlorobenzene were nitrated using HZSM-5 as a catalyst and liquid nitrogen dioxide as the nitrating reagent. When toluene is the substrate in this reaction, the reaction proceeds as shown in Equation 2.24 and the results of this report are presented in Table 2.14.



(2.24)

As shown in Equation 2.24, many different compounds are formed during this reaction. The isomers of nitrotoluene are the major products formed during the reaction, with phenylnitromethane, benzaldehyde and dinitrotoluene formed only in trace amounts.

Based on the results presented in Table 2.14, it is clear that this method is highly selective for the formation of the *para*-isomer, with *ortho*/*para* ratios of 0.08 to 0.64 for nitrotoluene. In the absence of zeolite, the *ortho*/*para* ratio is 1.48. However, even though the reaction times for these experiments are long (22 hours), the overall yield of these compounds is very poor, although both the yields and the

para-selectivities of the nitration of toluene are improved when the amount of HZSM-5 used in the reaction is doubled. For the nitration of toluene in the absence of zeolite, the overall yield of the reaction is 1%. When the amount of zeolite present was 2 g, the yield increased to 11%. The poor overall yield is also seen when the ZSM-5 zeolite is exchanged by different cations such as bismuth, copper, iron, and zinc, with yields ranging from 6% when copper is used to 14% when bismuth is used.

Table 2.14. Yields and *ortho/para* Ratios of Reaction Products Formed During the Nitration of Toluene and Chlorobenzene using HZSM-5 Catalysts, Nitrogen Dioxide and Oxygen, According to H. Suzuki *et al.*[30]

Substrate	**Catalyst**	**Substrate (mmol)**	**Yield (%)**	***ortho/para* Ratio**
Toluene	-	4	1	1.48
	HZSM-5		11	0.30
	HZSM-5[a]		24	0.08
	BiHZSM-5		14	0.14
	CuHZSM-5		6	0.38
	FeHZSM-5		8	0.22
	ZnHZSM-5		11	0.64
Chlorobenzene	HZSM-5	49	9	0.09

[a] HZSM-5 catalyst = 4.0 g (used a double amount of catalyst).

Other attempts at nitration were also made using toluene and zeolite Hβ containing silicon to aluminum ratios of 25 and 150 (data not shown).

Other attempts at nitration were also made using toluene and zeolite Hβ containing silicon to aluminum ratios of 25 and 150 (data not shown).

Using zeolite Hβ in the nitration of toluene instead of HZSM-5 did not result in an increase in either the overall yield of nitrotoluene or an increase in the *para*-selectivity of the reaction. The poor overall yields and the long reaction time needed to produce nitrated toluene or chlorobenzene make this method undesirable for general use.

2.1.6.2.3 Aromatic nitration using zeolite Hβ and nitrogen dioxide

Zeolite Hβ has also been used in aromatic nitration reactions in the gas phase. Use of this zeolite for gas phase nitration reactions was reported by Salakhutdinov *et al.*[31] In their experiments, chlorobenzene was nitrated using zeolite Hβ as the catalyst and nitrogen dioxide as the nitrating reagent.

A sample of catalyst was placed in a 30 ml capacity, flow type Pyrex reactor. Calcination of the catalyst was accomplished by heating the catalyst in the tube to 500 °C and maintaining the temperature for two hours. Following calcination, the catalyst was cooled to room temperature. Once at room temperature, nitrogen dioxide was passed through the catalyst in a stream of air at a delivery rate of 0.10-0.50 grams/hour. The catalyst was exposed to the nitrogen dioxide/air stream for two to five minutes. Then, vaporised chlorobenzene was passed through the catalyst in a stream of nitrogen carrier gas. At some point, the temperature of the system was increased to the reaction temperature, which ranged from 125 °C to 250 °C. However, the exact point in the procedure at which this occurred is not specified in

the original report. In addition, the reaction time for these experiments was not provided. The products of the reaction were condensed in three traps, at temperatures of 0 °C to -78 °C. The first trap was maintained at 0 °C; the second and third at -78 °C. The products of the reaction were analysed using gas chromatography. The results of these experiments are presented in Table 2.15.

As shown in Table 2.15, as the reaction temperature increases, so does the level of *para*-selectivity of the reaction, although the selectivity is high even at the lower temperature. In addition, a decrease in the proportion of *ortho*-nitrochlorobenzene, but a small increase in the proportion of *meta*-nitrochlorobenzene accompanies the increase in proportion of *para*-nitrochlorobenzene. However, in interpreting these data, the assumption has to be made that all other experimental variables have been held constant and that only the temperature varied.

Table 2.15. Reaction Temperature and Isomer Distribution from Nitration of Chlorobenzene Using Nitrogen Dioxide, Oxygen and Zeolite Hβ, According to Salakhutdinov *et al.*[31]

Catalyst Type	**Temperature (°C)**	**Isomer Distributions (%)**		
		ortho	***meta***	***para***
Zeolite Hβ[a]	125	7.7	0.4	91.8
Zeolite Hβ	150	2.7	0.7	96.6
Zeolite Hβ	200	2.4	1.4	96.2

[a]The silicon to aluminum ratio was not provided for the zeolites that were used as catalysts in this series of experiments.

A major drawback in attempting to interpret these data is that little information regarding reaction times or conversion of reactant is available. The only

information that has been provided with regard to overall yield of nitrochlorobenzenes is that the highest yield obtained was 38%. However, it is not specified which experiment produced these results.

These researchers also looked at the effects of temperature on the nitration of toluene and chlorobenzene using HZSM-5 catalyst. The procedure was conducted as before, and reaction temperatures ranged from 125 °C to 250 °C. The results of these experiments are presented in Table 2.16.

In these experiments, an increase in temperature leads to a small decrease in the amount of *para*-nitrated compound and a significant increase in the amount of *meta*-nitrated compound. When toluene is used as the substrate, the amount of *ortho*-nitrated compound decreases from 43% at a reaction temperature of 125 °C to 25% at a reaction temperature of 250 °C. The amount of *meta*-nitrated compound increases from 10% at 125 °C to 31% at 250 °C. In the case of chlorobenzene, the amount of *ortho*-nitrochlorobenzene produced is about the same at all of the reaction temperatures. There is an increase in the amount of *meta*-nitrochlorobenzene produced from 1% at 125 °C to 15% at 250 °C. From these data, again recognising that the interpretation is subject to the same types of limitations discussed before with regard to lack of information about conversion, *etc.*, it seems that when HZSM-5 is used as the catalyst and the reaction temperature increases, the nitration reaction becomes less specific with less *para*-nitrated product and more *meta* substituted product. This was not the case when zeolite Hβ was used as the reaction catalyst. In addition, 11% yield was the highest yield of nitrotoluenes obtained during these experiments, and, again, it is not specified which experiment produced these results.

Table 2.16. Reaction Temperatures and Isomer Distributions for Nitration of Toluene and Chlorobenzene Using Nitrogen Dioxide, Oxygen and Zeolite HZSM-5, According to Salakhutdinov *et al.*[31]

Substrate Type	**Catalyst Type**	**Temperature (°C)**	**Isomer Distribiution (%)**		
			ortho	***meta***	***para***
Toluene	HZSM-5	125	43	10	47
	HZSM-5	150	40	12	48
	HZSM-5	175	39	17	46
	HZSM-5	200	33	21	46
	HZSM-5	225	29	25	46
	HZSM-5	250	25	31	44
Chlorobenzene	HZSM-5	125	13	1	86
	HZSM-5	150	14	3	79
	HZSM-5	200	13	8	76
	HZSM-5	250	12	15	73

Based on these results, it appears that zeolite Hβ is the better catalyst to use in this nitrating system when *para*-substituted nitro compounds are the desired reaction products.

Because of the limitations in the data, it is difficult to determine the overall effectiveness of this system in nitrating aromatic compounds. However, in light of the fact that the highest yields obtained in these experiments were only 11% and 38%,

this system does not appear to be very effective in producing high yields of nitro compounds with a high degree of regioselectivity for the *para*-nitrated isomer.

2.1.6.2.4 Sulfuric acid and nitrogen dioxide system

C. Lin reported an experimental protocol by which benzene and toluene could be nitrated using sulfuric acid and nitrogen dioxide.[32]

In Lin's work, the following parameters were varied: the amount of substrate used, the reaction time, the reaction temperature, the flow rates of nitrogen and nitrogen dioxide gases, and the number of moles of sulfuric acid used. The different experimental parameters used are presented in Table 2.17.

Table 2.17. Different Experimental Parameters Used for the Nitration of Benzene and Toluene Using Nitrogen Dioxide and Sulfuric Acid as the Nitrating Reagent According to the Work of Lin.[32]

Substrate	Substrate (mmol)	Time (h)	Temp. (°C)	N_2 (ml/min)	NO_2 (ml/min)	H_2SO_4 (mmol)
Benzene	2000	4	70	130	70	148
Benzene	2000	8	72	130	130	352
Toluene	200	5	80	70	130	34

The aromatic compound and sulfuric acid were placed in a 250 ml, four necked, round bottomed flask equipped with a gas inlet, a stirrer, a condenser, and a thermometer. The benzene-sulfuric acid mixture was purged with nitrogen gas and the temperature was increased with stirring. The desired reaction temperature varied from 70 °C to 80 °C.

Once the desired temperature had been reached, nitrogen gas and nitrogen dioxide gas were bubbled into the solution through the gas inlet.

The reaction time varied from four hours to eight hours and was measured from the time the mixture had reached the appropriate reaction temperature and the mixture of nitrogen and nitrogen dioxide gas had been introduced to the reaction mixture. During the reaction time, the temperature was held constant, and the mixture of nitrogen and nitrogen dioxide gas was continuously introduced to the reaction mixture, with no change in the original flow rate. The reaction mixture was cooled to about 20 °C at the end of the reaction time. The brown to reddish coloured layer that formed during the course of the reaction was separated from the other components of the reaction mixture. Once extracted, it was washed with saturated sodium chloride solution. Then, the mixture was dried using anhydrous magnesium sulfate. The yield of nitrated aromatic varied from experiment to experiment, and the products were analyzed using nuclear magnetic resonance spectroscopy (NMR).

In the nitration of benzene when the reaction time was four hours, 91% of the benzene was nitrated. In the experiment in which benzene was used as the substrate with a reaction time of eight hours, the yield of nitrated benzene was 97%, a value not significantly different from that obtained when lower reaction time, temperature, flow rate of gases, and amount of sulfuric acid were used. The total percent yield of toluene was not reported, although the proportions of the *ortho*, *meta*, and *para*-isomers were reported as 58.8%, 4.9%, and 36.3%, respectively. Since the overall yield of nitrated toluene was not reported, it is difficult to assess the efficiency of this system for the nitration of toluene.

However, based on the data reported, the *para*-selectivity of the reaction was not better than that seen when the mixed acid system is employed for the nitration of toluene. In the mixed acid system, the *para*-selectivity for the nitration of toluene is 41%.[32]

2.1.6.2.5 Aromatic nitration using a phosphorus-vanadium oxide catalyst and nitrogen dioxide

Nitration of aromatic compounds using nitrogen dioxide can also be accomplished using a catalyst composed of a phosphorus-vanadium oxide. Use of this catalyst with nitrogen dioxide in aromatic nitration reactions in the vapour phase was reported by Schumacher and Wang.[33]

In their system, the nitration reaction was carried out by passing nitrogen dioxide gas and a vaporised stream of aromatic compound over a fluidised bed reactor containing the phosphorus-vanadium oxide catalyst. The catalyst was packed into a stainless steel tube, then heated to a temperature high enough to maintain the aromatic compound in its vaporised form once it had been injected over the bed of catalyst. The range of temperatures to which the catalyst was heated was 175 °C to 225 °C. Once the catalyst had been packed and heated, it was pretreated with nitrogen dioxide gas until saturated. The vaporised aromatic compound was contained in a humidified stream of air and mixed with the nitrating reagent, nitrogen dioxide, prior to being charged to the reactor and coming into contact with the catalyst. Nitration of the aromatic compound took place in the reactor, then, the reaction products were collected and analysed using gas chromatography.

Schumacher and Wang examined the nitration of benzene, toluene, and chlorobenzene using this approach. Although their protocol was essentially the same for each of these compounds, their experimental conditions changed from experiment to experiment. The experimental parameters, yield and *para/ortho* ratio of the reaction products are shown in Table 2.18.

Table 2.18. Yields and *para/ortho* Ratio of Reaction Products Formed When Benzene, Toluene, and Chlorobenzene are Nitrated Using a Phosphorus-Vanadium Oxide Catalyst and Nitrogen Dioxide, According to Schumacher *et al.*[33]

Substrate	**Substrate (ml/min)**	**NO_2 (ml/min)**	**Time (min)**	**Temp. (°C)**	**Yield (%)**	***para/ortho* Ratio**
Benzene	82.5	50.90	-	175	100	-
Toluene	16.68	42.41	-	175	61.2	0.9
Chlorobenzene	15.80	68.73	50	200	100	2.5
Chlorobenzene	16.26	70.48	10	225	84.2	2.3
Chlorobenzene	18.62	68.49	9	175	89.7	2.6

As shown in Table 2.18, the yield of nitrated aromatic was high when benzene or chlorobenzene was used as the substrate. However, the yield of nitrotoluene, obtained when toluene was the substrate, was more moderate. Unfortunately, the reaction under these experimental conditions was only moderately selective for the *para*-isomer when chlorobenzene was used as the substrate, and when toluene was the substrate, selectivity for formation of the *para*-isomer was even lower.

Based on the results of their research, Schumacher and Wang proposed a stoichiometric equation for the nitration of aromatics when a phosphorus-vanadium oxide catalyst and nitrogen dioxide were used.[33] They proposed that, for every two moles of aromatic compound, three moles of nitrogen dioxide were required to produce two moles of nitrated aromatic compound. In addition to the two moles of nitrated aromatic compound that were produced, one mole of nitric oxide and one mole of water were also produced (Equation 2.25).

$$2Ar\text{-}H + 3NO_2 \longrightarrow 2Ar\text{-}NO_2 + NO + H_2O \qquad (2.25)$$

2.1.6.3 Dinitrogen pentoxide

As in most of the other nitrating systems that have been discussed, the nitronium ion, NO_2^+, is the nitrating species when dinitrogen pentoxide is used as the nitrating reagent. This has been confirmed by Raman spectroscopy of a solution of dinitrogen pentoxide and nitric acid.[34]

According to the Encyclopedia of Inorganic Chemistry (Vol. 5, 1994), dinitrogen pentoxide is colorless and sensitive to light. In the gas phase, dissociation of dinitrogen pentoxide occurs according to Equation 2.26.[25]

$$N_2O_5 \rightleftharpoons NO_2 + NO_3 \longrightarrow NO_2 + NO + O_2 \qquad (2.26)$$

When this dissociation occurs in strong anhydrous acids such as sulfuric acid, nitric acid, or phosphoric acid, nitronium ion is produced.[25]

Dinitrogen pentoxide can be produced by reacting nitric acid with diphosphorus pentoxide as shown in Equation 2.27.[19]

$$2HNO_3 + P_2O_5 \longrightarrow 2HPO_3 + N_2O_5 \qquad (2.27)$$

McGuire reported a method of producing dinitrogen pentoxide in which synthesis occurs through electrochemical means.[35] In this system, a solution of dinitrogen tetroxide, N_2O_4, and nitric acid, HNO_3, is used. When dinitrogen tetroxide is oxidized to dinitrogen pentoxide by electrochemical means, the overall cell reactions can be represented according to Equations 2.28 (anode reaction) and 2.29 (cathode reaction).[35]

$$2HNO_3 + N_2O_4 \longrightarrow 2N_2O_5 + 2H^+ + 2e^- \qquad (2.28)$$

$$2HNO_3 + 2H^+ + 2e^- \longrightarrow N_2O_4 + 2H_2O \qquad (2.29)$$

Recently, the use of dinitrogen pentoxide in aromatic nitration reactions has become the subject of interest for many inventors.[36] For example, dinitrogen pentoxide, the nitrating reagent, has been used with zeolites, an inorganic catalyst, to nitrate toluene.[37, 38] A comparison of the results obtained when different types of zeolites have been used with dinitrogen pentoxide to facilitate the nitration of 2-nitrotoluene is presented in Table 2.19. Zeolites H-mordenite and H-faujasite gave the highest

conversions and yields for nitration of 2-nitrotoluene for reaction times of 3 and 15 minutes.[37]

Although dinitrogen pentoxide is highly effective as a nitrating reagent, it is an unstable compound, and, as such, is very difficult to handle. Its sensitivity to light and heat, and its explosive properties, represent the primary disadvantages to its use in aromatic nitration reactions.[25]

Table 2.19. Nitration of 2-Nitrotoluene Using Dinitrogen Pentoxide, N_2O_5, with Different Types of Zeolites.[37]

Zeolite Type	**Time (Min.)**	**Conversion[a] (%)**	**Yield[b] (%)**
None	180	6	95
H-ZSM-5	90	7	96
H-mordenite	15	85	93
H-faujasite 780	3	88	95
H-faujasite 720	3	92	94
Na-faujasite	60	16	95

[a] Combined yields of 2,4-dinitrotoluene and 2,6-dinitrotoluene. [b] The sum of the yields of 2-nitrotoluene and dinitrotoluenes.

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CHAPTER (3)

Nitration of Halogenobenzenes Using Zeolites, Dinitrogen Tetroxide, and Oxygen

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Nitration of Halogenobenzenes Using Zeolites, Dinitrogen Tetroxide, and Oxygen

3.0 Introduction

The discussions presented in Chapter 2 focused on the more recent developments in the preparation of nitrated aromatic compounds, particularly toluene and halogenobenzenes. From this discussion, it is clear that more research is needed to develop this field of study further.

Virtually all of the methods discussed in chapter two had some disadvantages associated with their use. For example, when nitric acid or mixed acids were used to facilitate nitration, environmentally damaging compounds were produced. In some of the nitration methods in which nitration was conducted in solution, the yields and selectivity for the *para*-isomer were low. Alternatively, in other experiments where acetyl nitrate was used as the nitrating reagent, the likelihood of explosions was increased. In addition, there are also drawbacks in nitrating aromatic compounds in the gas phase. Nitration in the gas phase utilizes high temperatures, which leads to an increase in the level of danger associated with the use of these methods due to the increased risk associated with heating potentially explosive, temperature-sensitive nitro compounds to very high temperatures. Also, again, the yields and the selectivity of the reactions were often low.

The disadvantages associated with these methods make them very difficult to use in industrial applications. Ideally, it should be possible to design a method to

nitrate aromatic compounds safely while being inexpensive and environmentally friendly. In addition, the method should provide high yields of nitrated aromatic compound and should demonstrate a high degree of selectivity for the *para*-nitrated isomer. One of the goals of this research project was to design this type of method by which aromatic nitration could be conducted. The experimental approach, materials and methods, and the results obtained during the course of this first phase of the project will be presented in the subsequent sections.

3.1 Materials and methods

3.1.1 Experimental approach

In these experiments, the nitration of several aromatic compounds was attempted.

The optimal conditions for nitration of chlorobenzene were determined, *i.e.*, the time of the reaction, the amount of catalyst, the use of solvent *vs.* no solvent, recycling of the catalyst and use of different types of catalysts. Once these conditions had been established, they were used to attempt the nitration of different aromatic compounds, such as benzene, toluene, fluorobenzene, bromobenzene, and iodobenzene. The basic procedure was the same for all of these experiments, with the variable being examined changing from experiment to experiment. Any other changes with regard to sample analysis, *etc.* have been noted in each section. These experiments will be addressed under the heading "Nitration of Aromatic Compounds", where the basic protocol used will be presented, followed by a more detailed explanation of the actual conditions for each series of experiments.

3.1.1.1 Chemicals and materials

The following aromatic compounds were used as substrates in the aromatic nitration reactions: benzene, toluene, fluorobenzene, chlorobenzene, bromobenzene, and iodobenzene. The purity of the fluorobenzene, bromobenzene, and iodobenzene was 99%. The purity of the toluene, chlorobenzene, and benzene was 99.9%. The toluene used in the experiments was analytical grade. The chlorobenzene and benzene used were HPLC grade. No mention was made of the grade quality for fluorobenzene, bromobenzene, or iodobenzene, only the purity of the compounds being provided. The toluene used in these experiments was purchased from Fisher. All of the other aromatic compounds were purchased from Aldrich. The standards used in the analysis using gas chromatography were also purchased from Aldrich.

There were four solvents used in these experiments. Dichloromethane and chloroform were analytical grade chemicals and were purchased from Fisher. The other two solvents, 1,2-dichloroethane and nitromethane, were both HPLC grade chemicals and were purchased from Aldrich.

The aromatic compounds and the solvents were used as they were received. No additional processes were performed on them to render them suitable for use in these experiments.

Several catalysts were used in this study. Chromatographic silica, SiO_2, was purchased from Fisher. Zeolites Hβ, NH_4ß, Naß, NH_4Y, NaY, HZSM-5 and NH_4-mordenite were purchased from Zeolyst International (formerly PQ Zeolites Ltd.). Zeolite Kß was prepared by exchange of Hβ by Adam Musson in Prof. Keith Smith's laboratory at the University of Wales, Swansea, UK.[1]

Nitrogen dioxide gas was purchased from BOC Gases (EEC No. 2341264) and was used to prepare the liquid dinitrogen tetroxide used as the nitrating reagent in each experiment.

3.1.1.2 Preparation of liquid dinitrogen tetroxide

Liquid dinitrogen tetroxide was prepared prior to beginning each experiment. A glass tube was cooled to –11 °C in a cooling bath containing acetone and dry ice. Nitrogen dioxide gas was passed from the gas cylinder into the glass tubing. Upon cooling, the brown nitrogen dioxide gas condenses, forming liquid dinitrogen tetroxide, which was green in colour.

3.1.1.3 Nitration of aromatic compounds

The basic procedure for the nitration of aromatic compounds was as follows. The catalyst was calcined, then cooled to room temperature and placed in a round-bottomed flask (100 ml). The addition of catalyst was followed by addition of substrate, solvent, and octadecane, the internal standard, to the flask. The mixture was stirred at room temperature, then placed in an ice-water cooling bath where stirring continued. The mixture was cooled to 0 °C, then it was flushed with oxygen for 20 minutes. Liquid dinitrogen tetroxide was added quickly all at once to the stirring mixture, and the flask was connected to an oxygen gas balloon. The reaction mixture was maintained at 0 °C during the course of the experiment, and the reaction times varied from experiment to experiment. The mixture was continually stirred throughout the course of the reaction. The reaction mixture was filtered through a

medium porosity sintered glass funnel, and the filtrate was diluted with water. The solvent used in the original reaction mixture was used to wash the reaction flask and the catalyst, and the organic phase of the reaction was separated from the aqueous phase, then dried over magnesium sulfate. The conversion, yield, and distribution of the isomers were determined by gas chromatography using a Phillips PU 4400 gas chromatograph.

3.1.1.4 Analysis of reaction products using gas chromatography

The use of gas chromatography (GC) is widely accepted as an analytical method by which many different components of a mixture can be effectively separated, identified, and quantified. At the end of each experiment in this project, the reaction products were analysed using gas chromatography.

Analysis of the reaction products was accomplished using a 30 m Alltech capillary econo-cap carbowax column. The internal diameter of the column was 0.32 mm, and the film thickness was 0.25 μm. When used to analyse the reaction products, the instrument was operated in the splitless mode. Other operating conditions, such as the flow rates of the different gases and temperature information, are provided in Table 3.1.

Table 3.1. Analytical Parameters Used in the Analysis of Reaction Products Using Gas Chromatography.

Flow rate of helium gas	2 ml/minute
Flow rate of nitrogen gas	28 ml/minute
Flow rate of hydrogen gas	25 ml/minute
Flow rate of air	400 ml/minute
Initial temperature of column	40 °C
Length of time at 40 °C	0.2 minute
First ramp of temperature	10 °C/minute (for 2 minutes)
Second ramp of temperature	5 °C/minute (for 1 minutes)
Final temperature of column	180 °C
Length of time at 180 °C	2 minutes
Injection temperature	300 °C
Temperature of detector	300 °C

3.1.1.4.1 Mathematical treatment of data

The conversion of substrate to nitrated product, the yield of nitrated product, and the isomeric distribution of the *ortho*, *meta*, and *para*-isomers can all be determined using the data obtained from the gas chromatographic analysis. The mathematical treatment of the data begins by calculating the response factor, or R.F., for each compound based on the values obtained by analysing samples of standards that are commercially available. Once the R.F. values have been determined, it is

possible to determine the quantity of *ortho*, *meta*, and *para*-isomers present in the reaction mixture from each of the experiments performed throughout the course of this study. From this point, the isomeric distribution of the nitrated products, the yield of nitrated product, and the conversion of starting compound to nitrated product can be calculated. The details of each calculation are presented in the following sections.

3.1.1.4.1.1 Calculation of response factors (R.F.)

The method for calibration used to measure the response factors and the yields of the products in this type of reaction mixture was that described by Scott.[2,3] In this study, the R.F. values were determined by preparing a series of solutions. There were four individual solutions in each solution series. Each solution was composed of a known amount of octadecane, a non-reactive standard typically used in gas chromatography analyses, and a known amount of the aromatic compound to be analysed. Both the octadecane and the aromatic compound, *i.e.*, chlorobenzene, *ortho*-chloronitrobenzene, *meta*-chloronitrobenzene, or *para*-chloronitrobenzene, were solubilised in the solvent used for the reaction. Most of the nitration reactions in this study employed 1,2-dichloroethane as the solvent, so the solutions used for the determination of the R.F. value were also prepared in 1,2-dichloroethane. However, in those experiments in which another solvent was used, these solutions were prepared using the alternative solvent.

The solution was injected into the gas chromatograph and the areas of the peaks for each compound were recorded.

It was possible to calculate the response factor for the aromatic compound using Equation 3.1, based on using a known mmol amount of both aromatic compound and octadecane standard.

$$\text{R.F. aromatic compound} = \frac{\text{mmol of aromatic compound}}{\text{mmol of octadecane}} \text{ X } \frac{\text{peak area of octadecane}}{\text{peak area of aromatic compound}} \quad (3.1)$$

The R.F. value was then used to calculate the isomeric distribution of the nitrated products that were produced during the aromatic nitration reactions completed in this study.

3.1.1.4.1.2 Calculation of the isomeric distribution of nitrated products

The isomeric distribution of the reaction products from the experiments performed in this study was calculated by first determining the number of mmol present in the reaction mixture. The number of mmol was calculated by multiplying the response factor obtained from Equation 3.1 by the mmol of octadecane added either to the reaction mixture or to the reaction products in a known amount, and then by the peak area of the nitrated isomer presented in the gas chromatogram and dividing by the peak area of the octadecane in the same chromatogram. This formula is shown in Equation 3.2.

$$\text{mmol of nitrated isomer} = \text{R.F. of nitrated isomer X mmol of octadecane X} \frac{\text{peak area of nitrated isomer}}{\text{peak area of octadecane}} \quad (3.2)$$

Once the mmol of nitrated isomer has been determined for each of the three possible isomers, *i.e.*, *ortho*, *meta*, and *para*, this information is used to calculate the isomeric distribution of each of the reaction products using Equation 3.3. This provides a measure of the selectivity of the nitration reaction.

$$\text{Selectivity for isomer} = \frac{\text{mmoles of isomer}}{\text{total mmoles of all isomers produced}} \times 100 \qquad (3.3)$$

3.1.1.4.1.3 Calculation of total yield of nitrated product

The total yield of nitrated aromatics produced by the aromatic nitration reaction is calculated using Equation 3.4.

$$\text{Yield} = \frac{\text{mmol } \textit{ortho} + \text{mmol } \textit{meta} + \text{mmol } \textit{para}}{\text{mmol of starting chlorobenzene}} \times 100 \qquad (3.4)$$

3.1.1.4.1.4 Calculation of conversion of aromatic substrate

By determining the number of mmol of unreacted substrate by using Equation 3.2, the percent of aromatic substrate converted at the end of the reaction can be calculated using Equation 3.5.

$$\text{Conversion} = \frac{\text{mmol of aromatic substrate at start of reaction - mmol of unreacted substrate}}{\text{mmol of aromatic substrate used in the reaction}} \times 100 \qquad (3.5)$$

The percentage of the yield is always lower (or equal) than the percentage of the conversion. The conversion is the percentage of the starting material consumed and the yield is the percentage of the formed product.

The experimental error in the analytical method (G.C) was calculated by analysing a standard solution containing octadecane and *ortho*, *meta*, and *para*-nitrochlorobenzene. The calculated percentage error was 3 %.

3.2 Nitration of chlorobenzene

The goal of this portion of the current project was to nitrate chlorobenzene effectively with a high conversion, yield, and *para*-selectivity using liquid dinitrogen tetroxide. There were several different parameters to be considered and examined in this study. These included the reproducibility of the work previously performed by Suzuki *et al.* using $Fe(acac)_3$ as the reaction catalyst, evaluating the nitration reaction in the absence of catalyst, and evaluating the feasibility of using a different catalyst, zeolite Hβ (Si/Al =12.5). In addition, the effects of different types of solvents were evaluated, as were the effects of using different volumes of nitrating reagent in the reaction. The possiblility of recycling the zeolite for use in additional reactions was also examined, using two different recycling methods. Lastly, the nitration of chlorobenzene was evaluated using different type of catalysts, in the hope of elucidating the way by which catalysts assist in the facilitation of the nitration reaction. Each of these studies is discussed and the results obtained from the experiments presented in the following sections.

3.2.1 Studies of the effects of catalysts on the nitration of chlorobenzene

3.2.1.1 Nitration of chlorobenzene using $Fe(acac)_3$ catalyst

Nitration of chlorobenzene using $Fe(acac)_3$ was reported by Suzuki.[4] In an attempt to reproduce the results obtained by Suzuki for the nitration of chlorobenzene, his experiment was repeated. In this experiment, $Fe(acac)_3$ was the catalyst, chlorobenzene was the substrate, 1,2-dichloroethane was the solvent, and liquid dinitrogen tetroxide was the nitrating reagent. These were added to the round-bottomed flask in the following amounts, respectively: 0.356 g, 10 mmol, 30 ml, and 10 ml. The system was flushed with oxygen as previously described, the reaction was continued for either 36 hours or 48 hours at 0 °C, and the reaction products were analysed using gas chromatography. The reaction times for each experiment, the results from the experiments, and the results previously reported by Suzuki for the same reaction conditions are shown in Table 3.2.

Table 3.2. Comparison of Results Obtained when the Catalyst, $Fe(acac)_3$, is Used in the Nitration of Chlorobenzene.

Time	**Conversion**	**Yield**	**Isomer Distribution[b] (%)**		
(h)	**(%)**	**(%)**	***ortho***	***meta***	***para***
36[a]	100	93	32	<1	68
36	79	66	31	1	68
36	82	73	32	>1	67
48	100	93	32	<1	67

[a] Result of experiment reported by Suzuki *et al.*[4] [b] Calculated by quantitative GC.

According to Suzuki, the conversion of chlorobenzene was 100% when the reaction time was 36 hours. In addition, at 36 hours, he also reports a 93% yield, with isomeric distribution of 32%, <1%, and 68% for the *ortho*, *meta*, and *para* isomers, respectively. As shown in Table 3.2, these results were not reproducible in our laboratory when the same reaction time was used. In our laboratory, when the reaction time was 36 hours, the isomeric distribution of chloronitrobenzene was almost exactly the same as the distribution reported by Suzuki, however, the conversion and the yield were less when the reaction had proceeded for 36 hours. When the reaction time was increased to 48 hours, the conversion and yield were increased to 100% and 93%, respectively. These values are exactly the same as the values reported by Suzuki. In addition, the isomeric distribution of chloronitrobenzene when the reaction time was 48 hours was almost the same as the distribution reported by Suzuki when the reaction time was 36 hours.

From these data, it is clear that the system employed by Suzuki for the nitration of chlorobenzene using 1,2-dichloroethane and liquid dinitrogen tetroxide was reproducible and provided a good foundation upon which to base future work.

3.2.1.2 Nitration of chlorobenzene in the absence of catalyst

It is clear that chlorobenzene is nitrated very effectively when 1,2-dichloroethane and liquid dinitrogen tetroxide are used with $Fe(acac)_3$ present. It was assumed that the presence of $Fe(acac)_3$ in the reaction mixture would work to speed up the nitration reaction. Testing this assumption formed the basis of the next

phase of experiments, in which the nitration reaction was conducted in the absence of any catalyst.

In this series of experiments, chlorobenzene was reacted using 1,2-dichloroethane as the solvent and liquid dinitrogen tetroxide as the nitrating reagent. All of the experimental conditions outlined in part 3.2.1.1 remained the same, except that no $Fe(acac)_3$ was added to the flask. This experiment was performed twice, once using 48 hours as the reaction time, and once using 72 hours as the reaction time. The reaction time for each experiment and the data obtained from each experiment are shown in Table 3.3.

In the first experiment, the reaction time of 48 hours was selected since it had produced favourable results in the experiment in the presence of $Fe(acac)_3$. When the nitration was attempted for 48 hours in the absence of catalyst, the conversion of chlorobenzene was only 3%, and there was no evidence for production of nitrochlorobenzenes.

Table 3.3. Nitration of Chlorobenzene Using 1,2-Dichloroethane and Liquid Dinitrogen Tetroxide in the Absence of Catalyst.[a]

Time	**Conversion[b]**	**Yield[b]**	**Isomer Distribiution[b] (%)**		
(h)	**(%)**	**(%)**	***ortho***	***meta***	***para***
48	3	0	0	0	0
72	6	2	39	0	61

[a] All reactions were carried out with chlorobenzene (10.0 mmol), 1,2-dichloroethane (30 ml), and dinitrogen tetroxide (10 ml) at 0 °C. [b] Calculated by quantitative GC.

In an effort to improve the results, the reaction time was increased to 72 hours, with very little improvement. When the reaction continued for 72 hours, the conversion doubled from 3% to 6% and the observed yield of nitrochlorobenzenes increased from 0% to 2%.

Although the *para*-selectivity of the reaction was good (61%, about 36% higher than the amount of *ortho*-chloronitrobenzene that was produced), the yield was so low that it is apparent from these experiments that the presence of a reaction catalyst is extremely important if the nitration of aromatic compounds, specifically chlorobenzene, is to be accomplished in a reasonable length of time.

3.2.1.3 Feasibility study of using zeolite Hβ (Si/Al = 12.5) as the reaction catalyst for the nitration of chlorobenzene

Zeolite Hβ is a catalyst that has been used in different nitrating systems to catalyse the nitration of aromatic compounds.[5,6] It has been used, with varying degrees of success, with nitric acid, acetyl nitrate and trifluoroacetyl nitrate, and nitrogen dioxide. Specifically, when zeolite Hβ (Si/Al = 12.5) was used in aromatic nitration reactions with acetyl nitrate, the yield of the nitro product was greater than 99% for all of the aromatic compounds used as substrates.[6] These experiments were performed in Prof. Keith Smith's laboratory at the University of Wales, Swansea. Since the use of zeolite Hβ in aromatic nitration reactions had already been established within our laboratory, it seemed a reasonable choice to attempt aromatic nitration using this catalyst along with liquid dinitrogen tetroxide.

In this series of experiments, calcined zeolite Hβ (1.0 g, Si/Al = 12.5) was used in the reaction mixture, along with chlorobenzene (10 mmol), 1,2-dichloroethane (30 ml), and liquid dinitrogen tetroxide (10 ml). The experiment was performed twice, at a reaction temperature of 0 °C. The reaction time for one experiment was 48 hours, while the reaction time for the second experiment was 50 hours. The results are presented in Table 3.4.

In both experiments, the conversion and yield were close to quantitative. The isomeric distribution for chloronitrobenzene was exactly the same for both experiments. The results of these two experiments indicate that zeolite Hβ can be used quite successfully in the nitration of chlorobenzene.

Table 3.4. Conversion, Yield, and the Isomer Distributions of Nitrochlorobenzenes Formed when Zeolite Hβ is Used as the Catalyst in the Reaction.[a]

Time	**Conversion[b]**	**Yield[b]**	**Isomer Distribution[b] (%)**		
(h)	**(%)**	**(%)**	***ortho***	***meta***	***para***
48	98	95	14	<1	85
50	100	90	14	1	85

[a] All reactions were carried out with zeolite Hß (1.0 g), chlorobenzene (10.0 mmol), 1,2-dichloroethane (30 ml), and dinitrogen tetroxide (10 ml) at 0 °C. [b] Calculated by quantitative GC.

That being established, this catalyst was employed in the subsequent experiments that were performed for the purpose of establishing good experimental conditions for the nitration of chlorobenzene using the liquid dinitrogen tetroxide nitrating system. Then, once the experimental parameters had been established, the

efficiency of other catalysts in catalysing the nitration of chlorobenzene was examined, followed by attempts at nitrating other aromatic compounds.

3.2.1.3.1 Nitration of chlorobenzene using zeolite Hβ (Si/Al = 12.5) as the reaction catalyst and varying the length of the reaction time

At the point in time at which these experiments were embarked upon, several aspects of the experimental requirements were clear. First, a catalyst was absolutely necessary for the nitration of chlorobenzene if the reaction was to occur within a reasonable length of time. Second, zeolite Hβ (Si/Al = 12.5) was a suitable catalyst for the reaction when the reaction was allowed to proceed for about 48 hours. Third, the nitration reaction showed very high conversion and yield over such a time period. The next parameter to be established was with regard to the length of time the reaction needed to proceed to produce the highest amount of chloronitrobenzene with the highest degree of *para*-selectivity. For that reason, a set of experiments was conducted in which the reaction time for the nitration reaction was varied.

The purpose of this study was to examine the progression of the nitration reaction. It had already been established that the nitration reaction proceeded almost to completion when the reaction time was about 48 hours. The progression of the nitration reaction was therefore examined at 12 and 24 hours. The experiment was conducted by removing a sample from the reaction mixture after the reaction had proceeded for 12 hours, then allowing the reaction to continue to a total reaction time of 24 hours. At the end of the 24-hour reaction time, the reaction mixture was treated as described previously and the reaction products were analysed using gas

chromatography. This experiment was repeated for a second time, using the same time points for sample withdrawal. The results of these experiments are presented in Table 3.5.

From the results obtained in previous experiments, it was clear that the nitration reaction would go very close to completion when the reaction time was about 48 hours. In this study, the conversion was about 53% at 12 hours and 70% at 24 hours while yields of chloronitrobenzenes were about 45% at 12 hours and 57% at 24 hours. In comparison, the conversion and yield were about 98% and 95%, respectively, when the reaction time was about 48 hours. Interestingly, regardless of whether the reaction time was 12, 24, or 48 hours, the *para*-selectivity for the reaction in these experiments was virtually the same, regardless of the conversion and yield, and ranged from 83% to 85%.

Table 3.5. Conversion, Yield and Isomer Distributions at Different Times During the Reaction of Chlorobenzene with N_2O_4 over Zeolite Hß.[a]

Experiment	**Time**	**Conversion[b]**	**Yield[b]**	**Isomer Distribution[b] (%)**		
No.	**(h)**	**(%)**	**(%)**	***ortho***	***meta***	***para***
1	12	55	42	15	1	84
	24	70	51	15	<1	85
2	12	51	49	16	1	83
	24	72	63	14	1	85

[a] All reactions were carried out with zeolite Hß (1.0 g), chlorobenzene (10.0 mmol), 1,2-dichloroethane (30 ml), and dinitrogen tetroxide (10 ml) at 0 °C. [b] Calculated by quantitative GC.

Analysis of these results along with the results obtained in previous experiments indicates that the nitration reaction is rather slow and requires approximately two days to go to completion. In addition, changes in the reaction time do not have an impact on the *para*-selectivity of the reaction in any significant way. Based on these results, a reaction time of 50 hours was used for most of the subsequent experiments.

3.2.1.3.2 Nitration of chlorobenzene using different amounts of zeolite Hβ (Si/Al = 12.5)

In order to examine the effect of the quantity of the catalyst on the nitration of chlorobenzene, a series of experiments was conducted using different quantities of zeolite Hß (Si/Al = 12.5). Based on the previous set of experiments in which the nitration reaction was monitored at 12, 24, and 48 hours, a reaction time of 24 hours was selected for this series of experiments. The results of the previous experiments indicated that the nitration reaction was complete at about 48 hours. Since, in this series of experiments, the progress of the reaction was being monitored as the reaction continued in the presence of different amounts of catalyst, it was important that a reaction time be selected that allowed for the nitration of chlorobenzene to occur. At the same time, it was important that the reaction not go to completion or close to completion, as it had been shown to do when the reaction time was about 48 hours. A reaction time of 24 hours met both of these criteria.

The following quantities of zeolite Hβ (Si/Al = 12.5) were used: 0.5 g, 1.0 g, 1.5 g, and 2.0 g. In these experiments, chlorobenzene (10 mmol) was used as the

substrate, and 1,2-dichloroethane (30 ml) was used as the solvent, and liquid dinitrogen tetroxide (10 ml) was used as the nitrating reagent. The reaction time for each of these experiments was 24 hours at 0 °C, and the products of the reaction were analysed using gas chromatography. The results for this series of experiments are shown in Table 3.6.

The data obtained from these experiments indicate that as the amount of zeolite Hβ used in the reaction increases from 0.5 g to 2.0 g, the conversion also increases. When the quantity of zeolite Hβ used was 0.5 g, the conversion was 57%. In contrast, the conversion when the quantity of zeolite Hβ used was 2.0 g was 87%, a 30% increase.

Table 3.6. Conversion and Isomer Distributions of Nitrochlorobenzene Formed when Different Amounts of Zeolite Hβ are Used as the Reaction Catalyst. [a]

Zeolite Hß	**Conversion** [b]	**Isomer Distribution** [b] **(%)**		
(g)	**(%)**	***ortho***	***meta***	***para***
0.5	57	15	<1	84
1	72	15	<1	85
1.5	84	15	<1	84
2	87	15	<1	84

[a] All reactions were carried out with chlorobenzene (10.0 mmol), 1,2-dichloroethane (30 ml), and dinitrogen tetroxide (10 ml) at 0 °C. [b] Calculated by quantitative GC.

The conversion was lowest (57%) when the quantity of zeolite Hβ used was 0.5 g and highest (87%) when the quantity used was 2.0 g. The conversion was 72%

with 1.0 g of zeolite, and 84%, with 1.5 g of zeolite. These results are not entirely unexpected. By increasing the amount of zeolite Hβ present in the reaction, the number of pores in which the reaction can occur is also increased, allowing for increased absorption of the reactants into the catalyst. It seems reasonable to expect that when an increased amount of catalyst is used in the nitration reaction, the conversion of chlorobenzene to chloronitrobenzene should increase, and these are precisely the results obtained in these experiments.

Although the conversion increased as the amount of zeolite Hβ in the reaction mixture increased, the *para*-selectivity of the reaction remained basically the same, at 84% to 85%. The consistency of the *para*-selectivity of this reaction, regardless of the amount of zeolite Hβ present in the reaction mixture, can be explained by observing the properties of zeolite Hβ. In contrast to the *ortho* and *meta*-isomers, the *para* isomer of nitrochlorobenzene is the isomer that most easily fits into the pore of zeolite Hß. Thus, increasing the quantity of zeolite Hß in the reaction mixture leads to an increase in the number of pores and an increase in the conversion of chlorobenzene to chloronitrobenzene. However, increasing the amount of zeolite Hβ in the reaction mixture does not lead to a change in the pore size itself, leading to the production of the same level of *para*-selectivity for the reaction, regardless of the amount of zeolite Hβ that is present.

3.2.2 Solvent effects

3.2.2.1 Nitration of chlorobenzene using different types of solvent

Up to this point, the only solvent that had been used as the experimental parameters for the nitration of chlorobenzene were being established was 1,2-dichloroethane. This solvent had been selected because it had been used successfully in previous nitration experiments by Suzuki *et al.* Although the results obtained using this solvent have been very positive, the type of solvent used can have a dramatic effect on the yield and the product distribution of a given organic reaction.[7,8] With this in mind, the effects of different solvents on the nitration of chlorobenzene were examined.

Four solvents were used in these experiments: nitromethane, dichloromethane, 1,2-dichloroethane, and chloroform. The volume of solvent used in each experiment was 30 ml. As in the other experiments, a standard amount of zeolite Hβ (1.0 g) was used as the catalyst, chlorobenzene (10 mmol) was used as the substrate, and liquid dinitrogen tetroxide (10 ml) was used as the nitrating reagent. The reaction time for the experiments using dichloromethane, 1,2-dichloroethane, and chloroform was 48 hours at 0 °C. When nitromethane was used as the solvent, the reaction time was 50 hours at 0 °C. The results of these experiments are shown in Table 3.7.

The conversion and yields of chloronitrobenzene were very high when dichloromethane, 1,2-dichloroethane, or chloroform as used as the solvent. The same cannot be said of the results obtained when nitromethane was used as the solvent. When dichloromethane, 1,2-dichloroethane, and chloroform were used, the conversion was greater than 99%, with yields ranging from 91% when chloroform was used to 95% when either dichloromethane or 1,2-dichloroethane were used.

Table 3.7. Conversion, Yield, and Isomer Distributions Formed when Different Solvents are Used.[a]

Solvent Type	Time (h)	Conversion[b] (%)	Yield[b] (%)	Isomer Distribution[b] (%)		
				ortho	*meta*	*para*
CH_3-NO_2	50	72	48	12	1	87
CH_2Cl_2	48	100	95	14	<1	85
$(CH_2Cl)_2$	48	>99	95	14	1	85
$CHCl_3$	48	100	91	21	<1	78

[a] All reactions were carried out with zeolite Hß (1.0 g), chlorobenzene (10.0 mmol), solvent (30 ml) and dinitrogen tetroxide (10 ml) at 0 °C. [b] Calculated by quantitative GC.

However, when nitromethane was used as the solvent in the reaction, the conversion was only 72%, and the yield was 48%. In spite of the lower conversion and yield of chloronitrobenzenes seen when nitromethane was used as the reaction solvent, the *para*-selectivity of the reaction was as high as or higher than the *para*-selectivity obtained when dichloromethane or 1,2-dichloroethane was employed as the solvent. The proportion of *para*-nitrochlorobenzene produced when nitromethane, dichloromethane, or 1,2-dichloroethane as used in the reaction was 87%, 85%, and 85%, respectively, while using chloroform in the reaction produced the lowest percentage of *para*-chloronitrobenzene, 78%. The differences seen in both the overall yield and the level of *para*-chloronitrobenzene produced in these reactions could be related to the polarity of the solvents used in the reaction.

In looking at the yield and *para*-selectivity in this reaction system, it is clear that the use of nitromethane as solvent in the reaction produces the lowest yield of chloronitrobenzenes with the highest level of *para*-selectivity. In contrast, use of

chloroform as the reaction solvent produces one of the highest yields of chloronitrobenzenes with the lowest level of *para*-selectivity.

It may be that the solvent exerts an effect on the dinitrogen tetroxide, with some solvents allowing for an increased availability of nitrating species and other solvents inhibiting the formation of the nitrating species. Both of these tendencies would have an effect on the overall formation of nitrated product. However, based on the results of these experiments, it is very clear that the solvent that has been selected for use in this project, 1,2-dichloroethane, produces high conversion, yield, and *para*-selectivity in the nitration of chlorobenzene, making it an excellent choice for future aromatic nitration reactions.

3.2.2.2 Nitration of chlorobenzene using different volumes of 1,2-dichloroethane

In the previous experiments, 1,2-dichloroethane and dichloromethane were shown to produce the best conversions, yields, and *para*-selectivities in the nitration of chlorobenzene. 1,2-Dichloroethane was selected as the solvent for use in further aromatic nitration reactions. In previous experiments, the reaction mixture contained 30 ml of 1,2-dichloroethane, but whether or not 30 ml of solvent was the best volume to use in the reaction mixture had not been experimentally studied. For this reason, a series of experiments was conducted in which the amount of solvent used was varied.

Nitration experiments were performed using the following volumes of solvent: 5 ml, 10 ml, 15 ml, 20 ml, 25 ml, 30 ml, 35 ml, and 40 ml. In these experiments, zeolite Hβ (1.0 g, Si/Al = 12.5) was used as the catalyst, chlorobenzene (10 mmol) was used as the substrate, and liquid dinitrogen tetroxide (10 ml) was used

as the nitrating reagent. The reaction time for each experiment was 24 hours at 0 °C, then the reaction products were analysed using gas chromatography. The results for these experiments are shown in Table 3.8.

From these data, it is clear that increasing or decreasing the volume of 1,2-dichloroethane used in the nitration of chlorobenzene does not affect the *para*-selectivity of the nitration reaction. When 5 ml of 1,2-dichlorethane was used in the reaction mixture, the *para*-selectivity was 83%. When the solvent amount was increased to 40 ml, the *para*-selectivity was slightly increased to 85%.

Table 3.8. Results of Experiments to Examine the Effects of Different Volumes of 1,2-Dichloroethane Solvent on the Conversion and the Isomer Distributions Formed when Chlorobenzene is Nitrated Using Liquid Dinitrogen Tetroxide.[a]

Solvent Amount	**Conversion[b]**	**Isomer Distribution[b] (%)**		
(ml)	**(%)**	***ortho***	***meta***	***para***
5	66	16	1	83
10	57	14	1	85
15	52	14	1	84
20	60	14	1	84
25	54	14	1	85
30	67	14	1	85
35	51	14	1	85
40	54	14	<1	85

[a] All reactions were carried out with zeolite Hß (1.0 g), chlorobenzene (10.0 mmol), and dinitrogen tetroxide (10 ml) at 0 °C. [b] Calculated by quantitative GC.

The values for all other volumes of 1,2-dichloroethane are within the range of 83% to 85%, leading to the conclusion that no significant change in the *para*-selectivity of the reaction is achieved when the volume of 1,2-dichloroethane in the reaction mixture is varied. The conversion of chlorobenzene ranged from 51% to 67%, but in a random manner, rather than one that indicated a genuine dependence on the amount of solvent. Consequently, 30 ml of 1,2-dichloroethane was employed in subsequent experiments.

3.2.2.3 Nitration of chlorobenzene in the absence of solvent

Experimental systems in which no solvent was required or in which only a small volume of solvent was required would have an advantage over systems employing larger volumes of solvent, especially if the nitration reactions were to be scaled up for industrial applications. From the previous set of experiments, it was clear that using a smaller volume of 1,2-dichloroethane in the nitration of chlorobenzene had little effect on either the conversion or the *para*-selectivity of the reaction. At this point, therefore, the effects of abandoning the use of solvent altogether were investigated in a series of experiments employing no solvent.

In these experiments, zeolite Hβ (1.0 g, Si/Al = 12.5), chlorobenzene (10 mmol), and liquid dinitrogen tetroxide (10 ml) were reacted as described previously, using a 50 ml round bottomed flask as the reaction vessel instead of a 100 ml flask. The progression of the nitration reaction was evaluated at three different reaction times: 24 hours, 50 hours, and 72 hours. The results obtained are shown in Table 3.9.

From these results, it is clear that the nitration of chlorobenzene is accomplished in the absence of solvent, with approximately the same conversion, yield, and *para*-selectivity as was previously seen in reactions in which 1,2-dichloroethane was a component of the reaction mixture.

Table 3.9. Reaction Times, Conversion, Yield, and Isomer Selectivity when Chlorobenzene was Nitrated Using the Liquid Dinitrogen Tetroxide System in the Absence of the Solvent.[a]

Time (h)	Conversion[b] (%)	Yield[b] (%)	Isomer Distribution[b] (%)		
			ortho	*meta*	*para*
24	26	20	14	0	86
50	53	46	15	<1	85
72	>98	90	15	<1	84

[a] All reactions were carried out with zeolite Hß (1.0 g), chlorobenzene (10.0 mmol), and dinitrogen tetroxide (10 ml) at 0 °C. [b] Calculated by quantitative GC.

However, unlike in the previous experiments in which 1,2-dichloroethane was a reaction component, the reaction required three days to go to completion. After 50 hours, only 53% of the chlorobenzene had been converted to product, and the yield of chloronitrobenzenes was 46%, with a *para*-selectivity of 85%. This reaction time had previously been associated with a 100% conversion, 90% yield, and 85% *para*-selectivity. One interesting result from this series of experiments was that the rate of conversion of chlorobenzene to chloronitrobenzenes appeared to increase over time, rather than decrease. When the reaction had proceeded for 24 hours, the conversion was 26%. The conversion 26 hours later, at a reaction time of 50 hours, was 53%, a 27% increase. The rate of the reaction from 24 to 50 hours appeared to be almost the

same as the rate over the period from 0 to 24 hours. However, after 72 hours, the conversion was 98%, a 45% increase.

It is clear from these experiments that the reaction mixture was established, the presence of solvent is required if the nitration reaction is to be accomplished in a reasonable length of time.

3.2.2.4 Nitration of chlorobenzene using different volumes of dinitrogen tetroxide

Until now, all of the aromatic nitration reactions attempted employed 10 ml of liquid dinitrogen tetroxide. At this point, the effects of several different parameters on the nitration of chlorobenzene have been evaluated, and it is clear that the nitration of chlorobenzene is dependent on the whole system working together to produce high levels of conversion, yield, and *para*-selectivity.

One of the goals of this project was to design a process for the nitration of aromatic compounds which does not require the presence of mixed acids or nitric acid. At the same time, a high conversion, yield, and level of *para*-nitrated product were desired. As discussed in previous chapters, using dinitrogen tetroxide as the nitrating reagent in reactions in which aromatic hydrocarbons such as benzene and toluene were the substrates did not produce very favourable results. Results of those experiments showed that the nitration could be accomplished, but that the reaction was very slow.[9] From the experiments completed at this point in the present study, it was clear that when the volume of dinitrogen tetroxide used was10 ml the goals of producing a high yield of chloronitrobenzenes with a high *para*-selectivity were

accomplished. However, it was unknown whether or not this volume of dinitrogen tetroxide was the minimum amount of nitrating reagent needed to achieve these goals.

For that reason, a series of six experiments was begun in which the amount of dinitrogen tetroxide in the reaction mixture varied from a minimum volume of 2.5 ml to a maximum volume of 20 ml. The dinitrogen tetroxide was reacted with chlorobenzene (10 mmol) and zeolite Hβ (1.0 g, Si/Al = 12.5), in 1,2-dichloroethane (30 ml). The reaction time for this series of experiments was 24 hours at 0 °C, and the reaction products were analysed using gas chromatography. The results are shown in Table 3.10.

Table 3.10. Effects of Different Volumes of Liquid Dinitrogen Tetroxide on the Conversion and Isomer Selectivity in Chlorobenzene Nitration.[a]

N_2O_4 (ml)	Conversion[b] (%)	Yield[b] (%)	Isomer Distribution[b] (%)		
			ortho	*meta*	*para*
2.5	39	26	15	<1	84
5	42	33	15	<1	84
7.5	60	45	15	<1	84
10	66	50	16	<1	83
15	71	59	15	<1	84
20	75	66	15	<1	84

[a] All reactions were carried out with zeolite Hß (1.0 g), chlorobenzene (10.0 mmol), and 1,2-dichloroethane (30 ml) at 0 °C. [b] Calculated by quantitative GC.

From these results, it is clear that increasing the amount of dinitrogen tetroxide in the reaction mixture leads to an increase in both the conversion of chlorobenzene and the yield of chloronitrobenzenes.

When the volume of dinitrogen tetroxide used was 2.5 ml, the conversion was 39% and the yield of chloronitrobenzenes was 26%. These percentages changed significantly as the volume of dinitrogen tetroxide was increased to 20 ml. The conversion was then 75% and the yield was 66%. However, increasing the amount of dinitrogen tetroxide used in the nitration reaction did not change the *para*-selectivity. Regardless of whether the volume of dinitrogen tetroxide was 2.5 ml or 20 ml, the selectivity for *para*-chloronitrobenzene was 84%.

Increasing the volume of dinitrogen tetroxide used in the reaction to volumes greater than 10 ml did not produce a significant change in the conversion of chlorobenzene to chloronitrobenzenes. More significant changes in the conversion were evident when the volume of dinitrogen tetroxide in the reaction was increased from very small volumes. For example, when the volume of dinitrogen tetroxide used was 2.5 ml, the conversion was 39%. When 7.5 ml of dinitrogen tetroxide was used, the conversion was 60%, a 21% increase. A similarly dramatic increase, 24%, is evident when the volume of dinitrogen tetroxide was increased from 5 ml to 10 ml. As the volume of nitrating reagent increased, the differences in the conversion became much less dramatic. For example, when 15 ml dinitrogen tetroxide was used, the conversion was 71%. The conversion when 20 ml dinitrogen tetroxide was used was 75%, only 4% more than the conversion seen when 15 ml of nitrating reagent was used.

From the results of these experiments, it is clear that the highest yield of chloronitrobenzenes was produced when the greatest amount of dinitrogen tetroxide (20 ml) was used in the reaction mixture. However, the goal of these experiments was to determine the minimum amount of nitrating reagent needed in the reaction to produce a high yield, with high selectivity for the *para*-nitrated product. Previous experiments in which 10 ml of dinitrogen tetroxide had been used with the same amounts of substrate, solvent, and catalyst had produced conversions of 98% or higher when the reaction time was increased from 24 hours to 48 or 50 hours. In addition, other experiments in which the reaction time was 24 hours had produced a conversion level of 72% with 85% *para*-selectivity for the reaction, values very close to those obtained in these experiments in which 15 ml and 20 ml of dinitrogen tetroxide were used over the same reaction time. Although the progress of the nitration reaction over a long reaction time with 15 or 20 ml of dinitrogen tetroxide has not been monitored, the reaction cannot be enhanced significantly in terms of conversion, yield, and *para*-selectivity when the volume of nitrating reagent is increased. Therefore, the dinitrogen tetroxide does not need to be used in a quantity greater than 10 ml in this experimental system.

3.2.2.5 Nitration of chlorobenzene using 5 ml of dinitrogen tetroxide

In the previous set of experiments, use of small volumes of dinitrogen tetroxide resulted in low conversion of chlorobenzene. For example, when the volume of dinitrogen tetroxide employed in the reaction was 2.5 ml, the conversion after 24 hours was only 39%. When the volume of dinitrogen tetroxide used was 5

ml, for the same length of time, the conversion was 42%. However, when the volume of dinitrogen tetroxide used was 7.5 ml, the conversion was much closer to that obtained with 10 ml or more of dinitrogen tetroxide.

It is of interest to know why the conversion level is so low when smaller volumes of dinitrogen tetroxide are used. Two possibilities exist. First, the conversion could be low because of the short reaction time. In experiments in which 10 ml dinitrogen tetroxide was used, the reaction was not complete until the reaction time was increased to 50 hours. The short reaction time, coupled with the decreased volume of nitrating reagent, could have led to the low conversion. The other possibility is that the amount of dinitrogen tetroxide used in the experiment was simply not enough to allow for the complete conversion of chlorobenzene to chloronitrobenzene, regardless of the reaction time.

In an effort to determine which of these factors led to the low conversion seen in the previous experiments, a series of experiments was conducted in which the conversion of chlorobenzene to chloronitrobenzene was monitored using different reaction times. In this first series of such experiments, the volume of liquid dinitrogen tetroxide used in the experiment was decreased from 10 ml to 5 ml. Each experiment was set up using zeolite Hβ (1.0 g, Si/Al = 12.5), chlorobenzene (10 mmol), and 1,2-dichloroethane (30 ml). The reactions were allowed to continue for periods from 24 to 82 hours. The results are shown in Table 3.11.

Based on the results presented in Table 3.11, it is clear that it is possible to use a volume less than 10 ml of liquid dinitrogen tetroxide with substrate (10 mmol) and still obtain a high conversion of chlorobenzene to chloronitrobenzene.

Table 3.11. Conversion and Isomer Selectivity when Chlorobenzene is Nitrated Using Liquid Dinitrogen Tetroxide (5 ml) at Various Reaction Times. [a]

Time (h)	Conversion[b] (%)	Yield[b] (%)	Isomer Distribution[b] (%)		
			ortho	*meta*	*para*
24	42	32	15	1	84
50	68	64	16	<1	83
72	88	83	16	<1	83
82	98	91	16	<1	83

[a] All reactions were carried out with zeolite Hß (1.0 g), chlorobenzene (10.0 mmol), and 1,2-dichloroethane (30 ml) at 0 °C. [b] Calculated by quantitative GC.

Neither the yield nor the *para*-selectivity of the reaction is sacrificed when the amount of dinitrogen tetroxide used in the reaction is decreased. In fact, the yield when the reaction time was 82 hours, at 91%, was comparable to the yield obtained when the volume of dinitrogen tetroxide used was 10 ml and the reaction time was 48 hours. The *para*-selectivity at each reaction time also remained consistent, at 83-84%. From these data, it is clear that a reduction in the volume of liquid dinitrogen tetroxide used in the reaction is possible and can occur without detrimental effect on the conversion, yield, and *para*-selectivity of the nitration reaction.

However, although these factors are not impacted in a detrimental way, the efficiency of another aspect of the experimental system decreases when the lower volume of nitrating reagent is used. Specifically, decreasing the amount of nitrating reagent used in the experiment requires a significant increase in the reaction time needed if the conversion and yield of the reaction are to be maintained at the same levels seen when the volume of nitrating reagent used is 10 ml. A 50 hours reaction

time is required to obtain 100% conversion with high yields and *para*-selectivity in a 10 ml reaction. Although there is some benefit in terms of reducing the cost of the reaction if a lower volume of nitrating reagent is used, the trade-off is that the reaction takes even longer when a lesser volume of nitrating reagent is used. If given a choice between lowering the volume of nitrating reagent and increasing the reaction time, or increasing the volume of nitrating reagent and decreasing the reaction time, the latter is the more preferred option, both in terms of cost and productivity. For that reason, the volume of nitrating reagent used in subsequent experiments was 10 ml.

3.2.3 Efficacy of recycling zeolite Hβ (Si/Al = 12.5) in nitration of chlorobenzene

As a catalyst, zeolite Hβ (Si/Al = 12.5) should be able to be reused many times to help promote the occurrence of nitration reactions. A series of experiments was embarked upon in which zeolite Hβ (Si/Al = 12.5) was reused several times in the nitration of chlorobenzene.

There were two aspects of the reuse of catalysts that were examined in this study. In the first, the zeolite was calcined prior to reuse in subsequent experiments. In the second, the zeolite was not calcined prior to reuse. Rather, it was dried to a powder using vacuum filtration and dried in air at room temperature for one hour, then used to catalyse the reaction.

3.2.3.1 Recycling of zeolite Hβ (Si/Al = 25) through calcination

A catalyst is a compound that is used to facilitate a chemical reaction. It is not part of the overall stoichiometry of the reaction, and it is recovered in its original formula after the reaction is complete.[10] In addition, because the catalyst does not take participate in the reaction and because it is regenerated in its original form, it should be able to catalyse additional reactions once the first reaction has been completed. However, the efficacy of recycling zeolite Hβ and using it in additional reactions had not been established.

In order to examine the effects of catalyst recycling on aromatic nitration reactions, a series of experiments in which the zeolite Hβ was first used to catalyse the nitration of chlorobenzene, then reused to evaluate its effectiveness in catalysing additional reactions, was undertaken.

The nitration procedure used was the same as outlined in the previous sections. Calcined zeolite Hβ (1.0 g) was used as the catalyst, chlorobenzene (10 mmol) was used as the substrate, 1,2-dichloroethane (30 ml) was used as the solvent, and liquid dinitrogen tetroxide (10 ml) was used as the nitrating reagent. Unlike the previous experiments, octadecane was not added to the reaction mixture. Instead, it was solubilized in 1,2-dichloroethane, then added to the reaction products as a standard in a known amount. The reaction time was 50 hours, after which the chloronitrobenzene was removed and analysed using gas chromatography.

In previous experiments, the zeolite had been discarded upon completion of the experiments. In this series of experiments, the zeolite used in the reaction was washed with 100 ml 1,2-dichloroethane and dried in the air for one hour. Then, the zeolite was re-calcined at a temperature of 550 °C for 24 hours. It was removed from

the oven and placed in the 100 ml flask, cooled to room temperature, then weighed. The weight was recorded, and the experiment outlined above was repeated. The same amount of chlorobenzene, solvent, and nitrating reagent was used in the reaction; only the amount of zeolite was altered. As in the first experiment, the reaction time was 50 hours, then the reaction mixture was analysed for the presence of chloronitrobenzenes.

Following the analysis, the zeolite was re-calcined as outlined above, then the experiment was repeated. This process was repeated for a total of nine re-calcinations. The results are shown in Table 3.12.

However, the tenth experiment (zeolite that had been re-calcined nine times) was conducted in a slightly different manner.

The whole reaction mixture was worked-up at the end of 92 hours. Samples of the reaction mixture from each of the time points, as well as at the end of the 92 hours reaction period were analysed using gas chromatography. The results for these experiments are shown in Tables 3.13 and 3.14.

As shown in Table 3.13, the conversion and the yield decreased as the number of recalcinations of the zeolite Hβ increased. The highest conversion was 100% with a 90% yield, and this was obtained from the very first experiment.

In subsequent experiments, both the conversion and the yield decreased. The decrease in the conversion and yield could be the result of the decreasing amount of zeolite Hβ catalyst present in the reaction mixture.

Table 3.12. Conversion, Yield, and Isomer Selectivity of Nitrochlorobenzene Formed Using Calcinated Zeolite Hβ (Si/Al = 12.5) and Re-calcined Zeolite Hβ (Si/Al = 12.5).[a]

Entry Number	Re-calcined Times	Conversion[b] (%)	Yield[b] (%)	Isomer Distribution[b] (%)		
				ortho	*meta*	*para*
1	0[c]	100	90	14	<1	85
2	1	92	89	14	<1	85
3	2	95	89	15	<1	84
4	3	91	84	16	<1	83
5	4	90	87	14	<1	85
6	5	85	80	14	<1	85
7	6	77	69	13	<1	86
8	7	81	71	13	<1	86
9	8	78	67	13	<1	86

[a] All reactions were carried out with chlorobenzene (10.0 mmol), dinitrogen tetroxide (10 ml) and 1,2-dichloroethane (30 ml) at 0 °C. [b] Calculated by quantitative GC. [c]This is the first experiment using calcined zeolite. Upon completion of the reaction, the zeolite was dried and calcined at 550 °C for 24 hours prior to reuse. Cycles 2-9 were performed using the same zeolite used in the first column entry, but the zeolite was recalcined before use.

The actual amount of zeolite Hβ used in each experiment is shown in Table 3.13.

As shown in Table 3.13, the amount of zeolite Hβ decreased by about 0.01 g each time it was recalcined and used in another experiment. This loss is not due to vaporisation of the catalyst or by the conversion of the catalyst into another compound.

Table 3.13. Mass of Zeolite Hβ (Si/Al = 12.5) Used in Repeat Use Experiments After Calcination at 550 °C for 24 h.

Entry Number	Number of ReCalcinations of Zeolite	Amount of Zeolite Hβ in Reaction Mixture (g)
1	0[a]	1.0490
2	1	1.0343
3	2	0.9995
4	3	0.9739
5	4	0.9507
6	5	0.9420
7	6	0.9078
8	7	0.8815
9	8	0.8603
10	9	0.8470

[a]This is the first experiment using calcined zeolite. Upon completion of the reaction, the zeolite was dried and calcined at 550 °C for 24 h prior to use. Cycles 2-10 were performed using the same zeolite used in the first column entry, but the zeolite was recalcined before use.

Rather, this loss can be attributed to the filtration process by which the zeolite is isolated from the reaction mixture at the end of the reaction. Although every attempt was made to recover all of the zeolite Hβ once the experiment was complete, it was not possible to make a complete recovery of the catalyst following the reaction, resulting in a slight decrease in the amount of catalyst used in subsequent experiments.

Table 3.14. Conversion, Yield, and Isomer Distributions of Nitrochlorobenzenes Formed when Recalcined Zeolite Hβ (Si/Al = 12.5) is Used as the Reaction Catalyst.

Time (h)	Conversion[b] (%)	Yield[b] (%)	Isomer Distribution[b] (%)		
			ortho	*meta*	*para*
24[a]	43	28	15	<1	84
50	72	56	15	<1	84
72	92	71	14	<1	85
92	98	92	15	<1	84

[a] The zeolite Hβ catalyst used in this experiment is the same zeolite used in entry number 10 in Table 3.12. The zeolite was recalcined for a total of nine times prior to its use in this experiment. The amount of zeolite Hβ used in this experiment was 0.8470 g. [b] Calculated by quantitative GC.

Based on the results of these experiments, it is clear that the zeolite Hβ can be reused many times without adverse effects on the percentage conversion and percentage yield of chloronitrobenzene. In addition, the *para*-selectivity of the reaction remained within the range of 83% to 85% throughout the series of experiments.

However, it is worthwhile to note that the efficiency of the zeolite in catalysing the nitration reaction decreases when the zeolite has been recalcined more than four times. This decrease in catalytic efficiency cannot necessarily be related to the amount of catalyst present during the reaction. For example, when the amount of zeolite Hβ used was 1.0490 g, the conversion and yield were 100% and 90%.

When the zeolite Hβ had been recalcined four times, entry number 5 in Table 3.12, the amount of zeolite used in the reaction had decreased to 0.9507 g. This represents a decrease of about 10% from the original amount of zeolite Hβ used in the

reaction. The conversion of chlorobenzene also decreased by about 10%. In general, the yields did not vary significantly as the amount of zeolite Hβ present in the reaction mixture dropped from 1.0490 g to 0.9507 g, with values ranging from 84% to 90%.

However, as the number of recalcinations increased, the amount of zeolite Hβ used in the reaction continued to decrease by about 0.01 g per experiment. This drop in the amount of zeolite used in the reaction was accompanied by a much steeper drop in the conversion and yield than was seen when the zeolite had been recalcined four times or less. For example, when the zeolite Hβ had been recalcined eight times, entry number 9 in Table 3.12, the amount of zeolite in the reaction was 0.8603 g, about 18% less than the amount of zeolite Hβ used in the first experiment. The 18% drop in the amount of zeolite Hβ in the reaction was accompanied by a 22% drop in the conversion of chlorobenzene, with a 23% decrease in the yield of chloronitrobenzenes. As the number of recalcinations increased, the conversion began to decrease at an even higher rate than the decrease in the amount of zeolite present in the reaction. From these data, it is clear that maintaining the same experimental conditions while, at the same time, continuing to recycle and reuse the zeolite catalyst results in a decrease in both the conversion and the percentage yield of chloronitrobenzenes.

However, while the efficiency of zeolite Hβ is decreased when the reaction time for the experiment remains at 50 hours, increasing the reaction time results in an increase in the conversion and yield of nitrochlorobenzenes, as shown in Table 3.14.

In this experiment, zeolite Hβ that had been recalcined nine times was used as the catalyst. The amount of zeolite Hβ present in the reaction was 0.8470 g, a 20% decrease from the amount originally present in the first set of experiments, shown in entry number one in Table 3.12. Since the results of the previous experiments had indicated that the efficiency of the zeolite Hβ in catalysing the nitration reactions decreased as the number of times the zeolite was reused increased, the progression of the nitration reaction was monitored in this experiment. Not surprisingly, when the reaction time was 24 hours, the conversion and yield were both very low, 43% and 28%, respectively. When the reaction time was 50 hours, the same reaction time that was used in the experiments recorded in Table 3.12, the conversion was 72%, with a yield of chloronitrobenzenes of 56%. The conversion seen in this experiment was 28% less than the conversion seen in the first experiment, the results of which are shown in entry number one in Table 3.12. The yield of chloronitrobenzenes was 34% less than the yield seen in the same experiment. However, as the reaction time increased, so did the conversion and yield, with values of 92% and 98% for conversion when the reaction times were 72 hours and 92 hours, respectively, and yields of 71% and 92% for the same experiments. In fact, the conversion of chlorobenzene to chloronitrobenzene when the reaction time was 92 hours and recalcined zeolite Hβ was used was almost the same as the conversion seen when the zeolite Hβ had not been recycled. Furthermore, the yield was actually 2% higher than the yield obtained in the experiment represented in entry number one in Table 3.12 when non-recycled zeolite Hβ was used as the reaction catalyst.

From these data, it is clear that the zeolite Hβ can be reused many times without affecting its ability to catalyse the nitration of chlorobenzene effectively, although its efficiency decreases somewhat as the number of times the zeolite is recycled increases. However, this decrease in effectiveness can be overcome by altering the experimental conditions under which the nitration reaction occurs.

3.2.3.2 Recycling zeolite without calcination

In the previous experiments, zeolite Hβ was used in a nitration experiment, then recalcined prior to use in subsequent experiments. Although recalcination is an effective method by which the zeolite can be cleaned and recycled, this process requires a large amount of time. In this series of experiments, an alternative method of zeolite regeneration was attempted in which the zeolite that had been used in a nitration experiment was isolated by vacuum filtration.

The first experiment in this series used calcined zeolite Hβ (1.0 g, Si/Al = 12.5) as the reaction catalyst. The zeolite was reacted with chlorobenzene (10 mmol), 1,2-dichloroethane (30 ml), and liquid dinitrogen tetroxide (10 ml). The reaction time was 50 hours at 0 °C. As in the previous experiments, the reaction products were isolated and analysed using gas chromatography.

Once the first experiment was completed, the zeolite catalyst was isolated and dried to a powder under reduced pressure. Then, the zeolite was left to dry in air at room temperature for one hour. Then, the zeolite was used again to catalyse another nitration reaction, without the calcination process that was applied to the zeolite in the previous series of experiments. The air-dried zeolite was placed into the reaction

vessel and weighed. The mass was recorded and the same amounts and volumes of substrate, solvent, and nitrating reagent were reacted together. As in the first experiment, the reaction was continued for 50 hours at 0 °C, then the reaction mixture was separated and analysed as described previously.

Upon completion of each experiment, the zeolite Hβ was recovered, the drying process was repeated, and the catalyst was reweighed, then used in another experiment. This process was repeated for a total of seven times. The results for these experiments are shown in Table 3.15.

In this experiment, reusing the zeolite over several experimental cycles resulted in lower levels of conversion and yield. In addition, the selectivity of the reaction, which in previous experiments had been in the range of 83% to 85% or higher for the *para* nitrated product, showed a significant decrease. Since the previous experiments had shown that recycling the zeolite did not produce seriously adverse affects on the ability of the zeolite to catalyse reactions effectively while still maintaining a high degree of *para*-selectivity of the reaction products, these results may seem a little puzzling.

However, as mentioned previously, the zeolite was weighed before it was used in each experiment. The data obtained from weighing the zeolite are presented in Table 3.16, and the analysis of these data may help to explain the results of this experiment.

In the first recycling study, the mass of the zeolite catalyst decreased by about 0.01 g each time the zeolite was used. In this study, the mass of the zeolite increases over the amount originally used in the first experiment.

Table 3.15. Conversion, Yield, and Isomer Distributions of Nitrochlorobenzenes Formed Using Zeolite Hβ (Si/Al = 12.5) Recycled and Dried by Vacuum Filtration and Air Drying.[a]

Entry No.	Recycled Times	Conversion[b] (%)	Yield[b] (%)	Isomer Distribution (%)		
				ortho	*meta*	*para*
1	0	100	93	15	<1	84
2	1	96	86	24	<1	75
3	2	95	81	30	<1	69
4	3	96	90	36	1	63
5	4	94	86	37	1	62
6	5	91	80	37	1	62
7	6	85	78	35	1	64
8	7	83	77	35	1	64

[a] All reactions were carried out with chlorobenzene (10.0 mmol), dinitrogen tetroxide (10 ml) and 1,2-dichloroethane (30 ml) at 0 °C. [b] Calculated by quantitative GC.

The pattern of increasing weight is interesting in that the weight of the zeolite increases from 1.0320 g in the first experiment, entry number one in Table 3.16, to 1.5837 g, in entry number 5 in Table 3.16.

The weight of the zeolite then decreases to values ranging from 1.4109 g to 1.4586 g. This increase, then decrease can be explained in the following way.

In these experiments, the zeolite catalyst was dried in air. In the first set of recycling experiments, drying was followed by calcination of the zeolite at very high temperatures for 24 hours. The application of high temperatures to the zeolite resulted in the purification of the zeolite from any residual organic compounds,

nitrogen compounds and water that may have been trapped in the three dimensional zeolite structure.

Table 3.16. Mass of Zeolite Hβ (Si/Al = 12.5) After Vacuum and Air Drying.

Entry No.	Number of Times Zeolite has Been Recycled	Amount of Zeolite Hβ in Reaction Mixture (g)
1	0[a]	1.0320
2	1	1.3302
3	2	1.5201
4	3	1.5335
5	4	1.5837
6	5	1.4129
7	6	1.4586
8	7	1.4109

[a]This is the first experiment using calcined zeolite. Upon completion of the reaction, the zeolite was dried using a vacuum first, then in air at room temperature for one hour. Cycles 2-8 were performed using the same zeolite used in the first column entry, but the zeolite was dried before use.

In the absence of the application of high temperatures to the zeolite, the organic compounds and water were retained in the zeolite pores. The retention of these compounds in the zeolite resulted in the increased weight of the zeolite used in subsequent experiments. The increase in the mass of the zeolite used in the experiment is very clearly seen in the data presented in Table 3.16 for entry numbers two through five. But, as shown in entries six through eight, the mass of zeolite used in the reaction decreases when compared to the masses of zeolite used in entries three

through five. However, in all cases, the mass of zeolite used in the reaction is higher than the original amount of zeolite used in the first experiment. The apparent decrease shown in entries six through eight can be attributed to the natural loss of zeolite that occurs as the zeolite is continually recycled. This loss was evident in the first recycling study, and it also evident here, although it is not possible to tell exactly how much of the zeolite has been lost during the recycling process.

The retention of materials and water in the zeolite structure as the zeolite is continually recycled and reused has an adverse effect on the conversion, yield, and *para*-selectivity of the nitration reaction. In the first experiment, entry number one in Table 3.15, the conversion is 100% with a 93% yield. The *para*-selectivity of the reaction was 84%. These results are typical of the results obtained in previous experiments. However, as the number of times the zeolite was recycled and reused increased to seven, shown in entry number eight in Table 3.15, the conversion dropped to 83% with a 77% yield. The *para*-selectivity of the reaction decreased to 64%, with *ortho*-chloronitrobenzene comprising 35% of the chloronitrobenzene produced during the reaction. Occupation of the zeolite pores by other compounds apparently leads to a decrease in the number of acid sites within the zeolite structure at which the reaction can occur, causing the decrease in the conversion and yield of chloronitrobenzenes. In addition, the loss of *para*-selectivity in the course of the reaction can be attributed to the occupation of the zeolite pores by these compounds, causing more of the nitration reactions to occur on the surface of the zeolite rather than in the pores. When the reactions occur in the pores of the zeolite, the *para*-isomer is heavily favoured because of the spatial limitations offered within the pore

itself. However, when the reactions are not limited to the pore, and the nitration reaction occurs on the surface of the zeolite, the formation of the *ortho*-nitrated product is higher than would normally be produced by in-pore reactions.

From these results, it may be concluded that vacuum filtration and drying in air is not a suitable method for use in preparing recycled zeolite. Based on these observations, it is recommended that calcination of the zeolite be completed if recycling of zeolite is desired.

3.2.4 Use of different catalysts to promote nitration

When liquid dinitrogen tetroxide was used as the nitrating reagent for the nitration of chlorobenzene in the absence of catalyst, chlorobenzene was nitrated at very low levels, with conversions of 3% to 6% when the reaction times were 48 hours and 72 hours, respectively. The yields of chloronitrobenzenes were even lower, 0% and 2% for the same reaction times. In contrast, chlorobenzene was nitrated very effectively when liquid dinitrogen tetroxide was used as the nitrating reagent and zeolite Hβ was used as the reaction catalyst. In fact, the results of the previous experiments showed that the nitration reaction was very effective when the nitrating system had zeolite Hβ as one of its components, but not otherwise. Based on this observation, it is clear that the use of catalyst is important if the nitration reaction is to occur at a reasonable rate. However, how the catalyst works to effect the nitration reaction has not been established.

There are several different ways in which zeolite Hβ could be exerting an effect on the nitration reaction. It may be that the pore size of the zeolite is a

contributing factor. Or, it may be possible that the zeolite Hβ allows for the formation of intermediates that may not be formed under other experimental conditions or when other catalysts are used. Perhaps the zeolite Hβ allows for some surface reactions that are conducive to the nitration of chlorobenzene. Another alternative may be the degree of acidity produced by the zeolite Hβ, which could be modified by changing the silicon to aluminium ratio of the catalyst itself. While each of these factors may contribute to the effective nature of zeolite Hβ in the catalysis of aromatic nitration reactions, their individual effects had not been evaluated. For this reason, a series of experiments was undertaken in which different catalysts were used to catalyse the nitration of chlorobenzene. Each of the catalysts used as selected because it met very specific criteria, in the hopes that by evaluating and analysing the data generated from these experiments, more information could be obtained regarding how the catalysts contribute to the effectiveness of the aromatic nitration reaction.

In this series of experiments, the nitration of chlorobenzene was attempted using the same experimental procedure that had been used in the previous experiments. The catalyst (1.0 g) was reacted in a 100 ml round bottomed flask with chlorobenzene (10 mmol), 1,2-dichloroethane (30 ml), and liquid dinitrogen tetroxide (10 ml). The types of catalyst, the silicon to aluminium ratio, where applicable, of each type of catalyst, and the reaction time for each experiment are shown in Table 3.17.

The catalysts used in these experiments can be separated into five main categories. The first category is composed of the zeolites Naβ, Kβ, and NH_4β. Zeolites HY and NaY comprise the second group. The medium pore zeolites

HZSM-5 (Si/Al= 50) and HZSM-5 (Si/Al = 150) comprise the third group. H-mordenite and silica gel (SiO_2) each comprises their own group.

Table 3.17. Catalysts and Their Si/Al Ratios, and Reaction Times Used in Experiments to Evaluate the Effects of Catalyst on the Nitration of Chlorobenzene. [a]

Catalyst Type	**Si/Al Ratio**	**Reaction Time (h)**
Naβ	12	50
Kβ	12	50
NH_4β	12.5	50
HY	30	50
NaY	28	50
HZSM-5	50	72
HZSM-5	150	72
H Mordenite	10.5	50
SiO_2	-	50

[a] All reactions were carried out with catalyst (1.0 g), chlorobenzene (10.0 mmol), dinitrogen tetroxide (10 ml) and 1,2-dichloroethane (30 ml) at 0 °C.

As in the other experiments, the products of the reaction were analysed using gas chromatography upon completion of the reaction. The results for these experiments are shown in Table 3.18.

As shown in Table 3.18, the conversion, yield, and the *para*-selectivity of the nitration reaction varies from one catalyst group to another, as well as between members of a given catalyst group. In the case of the zeolite β, as the size of the

counter-cation increases there is a slight decrease in the conversion, yield, and *para*-selectivity of the reaction.

Table 3.18. Conversion, Yield, and Isomer Distributions in Nitration of Chlorobenzene Using Different Catalysts.[a]

Catalyst Types	Conversion[b] (%)	Yield[b] (%)	Isomer Distribution[b] (%)		
			ortho	*meta*	*para*
Naβ	100	96	15	0	85
Kβ	97	92	21	0	79
NH_4β	76	70	30	1	69
HY	100	91	16	2	82
NaY	100	91	16	1	83
HZSM-5	44	42	28	2	70
HZSM-5	48	32	20	<1	79
H-Mordenite	36	28	27	0	73
SiO_2	40	28	29	<1	70

[a] All reactions were carried out with catalyst (1.0 g), chlorobenzene (10.0 mmol), dinitrogen tetroxide (10 ml) and 1,2-dichloroethane (30 ml) at 0 °C. [b] Calculated by quantitative GC.

In the previous experiments, the counter-cation was a proton, and the conversion, yield and *para*-selectivity under similar conditions were 100%, 90%, and 85%, respectively. The results obtained when sodium, a larger cation, was used were almost the same, with 100% conversion, 96% yield, and 85% *para*-selectivity. As the cation size was increased, as when potassium was used, the conversion dropped to 97%, the yield to 92%, and the *para*-selectivity to 79%.

The worst results using a zeolite β catalyst were obtained when zeolite $NH_4\beta$ was used as the reaction catalyst. The conversion with this catalyst was only 76%, the yield was 70%, and the *para*-selectivity of the reaction was only 69%. However, the reason for this drop in conversion, yield, and *para*-selectivity is most likely due to the fact that zeolites Hβ, Naβ, and Kβ were all calcined prior to use, whereas zeolite $NH_4\beta$ was not calcined prior to use, simply because calcination of this zeolite results in the loss of ammonia, producing zeolite Hβ. The lack of calcination generally results in lower yields, conversion, and *para*-selectivity, as was shown in the previous study in which the efficacy of recycling the zeolite catalyst was examined. And, in fact, the results obtained when zeolite $NH_4\beta$ was used were very close to those obtained when zeolite Hβ was recycled and reused without calcination, as shown in Table 3.15, entry number 8. In this experiment, the conversion was 83%, only 7% higher than when zeolite $NH_4\beta$ was used. The yield was also 7% higher than when zeolite $NH_4\beta$ was used. Lastly, the *para*-selectivity of the reaction when zeolite $NH_4\beta$ was used was 5% higher than when recycled zeolite Hβ was used without calcination. All in all, the results obtained in the study in which the zeolite was not calcined are very close to the results obtained with zeolite $NH_4\beta$. This observation lends credence to the hypothesis that it was the lack of calcination of the zeolite which led to the low levels of conversion, yield, and *para*-selectivity seen when zeolite $NH_4\beta$ was used as the catalyst, rather than a problem with the catalyst itself.

The next group of catalysts that were examined involved zeolite Y with different counter-cations. The two cations used were proton and sodium. Although

the structure of zeolite Y catalysts is different from the structure of zeolite β, both types are large pore zeolites with three dimensional, non-linear structures. Although two different cation-exchanged forms of zeolite Y catalysts were used, they produced results that were almost exactly the same. The conversion and yield, when either of the zeolites was used, were 100% and 91%, respectively. Only minor differences were observed in the *meta*- and *para*-selectivity of the reaction. When zeolite HY was used as the reaction catalyst, 2% *meta*-chloronitrobenzene and 82% *para*-nitrochlorobenzene were produced. The results obtained for the *para*-selectivity of the reaction when zeolite NaY was used were almost the same. In this case, the percentage of *meta*-chloronitrobenzene was 1% and the percentage of *para*-chloronitrobenzene produced was 83%. In any case, the results obtained when the zeolites Y were used were almost the same as when zeolite Hβ was used, even though the structures of the two zeolites are different, as were their silicon to aluminium ratios and the acidity of each. The lack of significant differences in the results obtained when these two types of zeolites were used, despite their structural and chemical differences, indicates that neither of these two factors has a significant impact on the ability of the zeolite to catalyse the nitration reaction.

The same cannot be said, however, as one begins to evaluate the data obtained from the experiments in which the catalyst, HZSM-5, was used. HZSM-5 is a medium pore, three-dimensional zeolite that was calcined before use, and two samples with different silicon to aluminium ratios were employed. In the first experiment, the silicon to aluminium ratio was 50, while in the second, the silicon to aluminium ratio was 150. In both experiments, the reaction time was increased from

50 hours to 72 hours. The conversions were almost the same, 44% when the silicon to aluminium ratio was 50, and 48% when the silicon to aluminium ratio was 150. Although the results for the conversion were almost the same, there was a 10% difference between the yield produced when HZSM-5 (Si/Al = 50) was used and that when HZSM-5 (Si/Al = 150) was used. In both cases, the yield was low, with values of 42% when HZSM-5 (Si/Al = 50) was used and 32% when HZSM-5 (Si/Al = 150) was used. The *para*-selectivity of the reaction also decreased in comparison to the *para*-selectivity seen in reactions when zeolite Hβ (Si/Al = 12.5) was used in the reaction. When HZSM-5 (Si/Al = 50) was used, the *para*-selectivity of the reaction was 70%. The *para*-selectivity of the reaction was not much higher when HZSM-5 (Si/Al = 150) was used. In this case, the proportion of *para*-chloronitrobenzene was 79%.

The results of the experiments in which the HZSM-5 catalysts were used are a little more difficult to explain. There are two primary differences between the HZSM-5 catalysts and the zeolites β and Y. Zeolites β and Y are both large pore, three-dimensional catalysts, and all of the zeolites β and Y used in these experiments had silicon to aluminium ratios between 12 and 30. In contrast, the HZSM-5 catalysts are medium pore, three-dimensional catalysts, and the two catalysts used in this experiment had significantly higher silicon to aluminium ratios compared to the zeolites β and Y. Typically, a higher silicon to aluminium ratio results in a decrease in the number of acid sites in the catalyst. However, while the silicon to aluminium ratio is one factor that influences the acidity of the catalyst, it is not the only factor involved in this process, and, in fact, when a cation other than hydrogen is used, the

acidity of the catalyst decreases. In light of that, it is possible to evaluate the effects of acidity on the nitration of chlorobenzene when any of the zeolites β or Y were used that did not employ a proton as the cation.

In the previous results using zeolites β and Y, the conversion, yield and *para*-selectivity of the reaction were high, with the exception of when zeolite $NH_4\beta$ catalyst was used. Regardless of whether or not cations that would impart a decreased level of acidity on the catalyst, such as sodium or potassium, were used in the catalyst, this trend was evident.

However, in the case of the HZSM-5 catalysts, only moderate levels of conversion, yield, and *para*-selectivity of the nitration reaction were produced. This was true even though one of the catalysts used in the experiments, HZSM-5 (Si/Al = 50) had more acid sites than the other catalyst, HZSM-5 (Si/Al = 150). The HZSM-5 samples with the silicon to aluminium ratio of 150 produced a higher level of *para*-selectivity for the reaction products, possibly because of the process of dealumination, which would have opened up the pore structure of the zeolite, causing it to more closely resemble the larger pore systems. However, the yield obtained from this same catalyst was lower than that obtained from the HZSM-5 with the silicon to aluminium ratio of 50, possibly because of the lower density of effective catalytic sites available.

Based on these results, the degree of acidity of the catalyst seems to exert a minimal effect on the catalysis of the reaction. A greater degree of influence over whether or not the reaction proceeds seems to be determined by the pore size and the three dimensional nature of the catalyst. The larger pores of zeolites β and Y appear

to be better able to catalyse the nitration reaction, resulting in an increase in the conversion, yield, and *para*-selectivity.

The next catalyst that was studied was H mordenite. Mordenite is another large pore zeolite, in this case with a proton as the counter-cation. It was selected for use in this study because, instead of having a three-dimensional structure, this catalyst has a linear structure. In addition, the silicon to aluminium ratio in this catalyst is 10.5. The silicon to aluminium ratio coupled with the presence of hydrogen as the counter-cation should produce sufficiently acidic conditions to enhance the nitration reaction. By using this catalyst in which the pore size was the same (large pore) as zeolites β and Y but which differed from these two zeolite groupings with respect to its three dimensional structure, it was possible to evaluate the effects of the three dimensional structure of the catalyst on the effective catalysis of the nitration reaction.

When H mordenite was used, the conversion was very low, 36%, and the yield was even lower, 28%. The *para*-selectivity of the reaction was 73%. In fact, these results are even lower than those obtained when the HZSM-5 catalysts were used. However, the reaction time when H mordenite was used was only 50 hours; if the reaction had continued for an additional 22 hours, then the values for conversion, yield, and *para*-selectivity would probably have increased. Thus, the results when H mordenite was used to catalyse the nitration of chlorobenzene lead to the conclusion that the ability of the catalyst to catalyse the nitration reaction is primarily due to the dimensionality of the catalyst, rather than the pore opening. The larger cavities

created within the crystals of zeolites with three-dimensional pore structures permit greater mobility of the reaction partners within the pore structure.

It is interesting to note that the use of both the HZSM-5 catalysts and H mordenite resulted in lower *para*-selectivity, as well as lower yields than when the zeolites β and Y were used. The decreases in yield and selectivity may result from the more restricted diffusion through the catalyst pore, leading to increased competition from reactions taking place on the external surface of the solid.

As a comparison, the nitration of chlorobenzene when silica gel, SiO_2, was used in the reaction mixture was evaluated. When silica gel was used under comparable conditions, the conversion was 40%, with a yield of 28%, and the *para*-selectivity was 70%.

From the results of this study, it does not appear that the catalytic process relies upon strong acid catalysis, nor does it depend on the size of the cation in the catalyst. The best results were obtained when a large pore, three-dimensional catalyst was used in the reaction, and the nature of the cation present in the catalyst exerts only a small effect on the progress of the reaction. This small effect is evidenced by the fact that the zeolites containing a hydrogen, sodium, or potassium cation yielded very similar results for each reaction where comparison was possible. It may be that the role of the active site is merely to bring together the reagents and substrates within the confines of the pore by simple co-adsorption, thereby providing a more suitable environment in which the reactants and substrates can react. Another way by which the catalysts may act to assist in the nitration reaction is by facilitating the cleavage of

dinitrogen tetroxide to yield monomeric nitrogen dioxide, which has been suggested as the active reagent in vapour phase reactions.[11,12]

3.3 Nitration of benzene, toluene, and selected halogenobenzenes using zeolite Hβ (Si/Al = 12.5), 1,2-dichloroethane, and liquid dinitrogen tetroxide

During the course of the previous experiments, several different experimental parameters which influence the nitration of chlorobenzene were examined. These experiments showed that in some cases, changing the amounts of catalyst, substrate, solvent, and nitrating reagent used in the reaction resulted in an increase in the conversion, yield, and *para*-selectivity of the nitration reaction. However, these increases were not substantial enough to justify using increased amounts of reactants, solvent, or nitrating reagent. For this reason, the parameters used in the first set of experiments, *i.e.*, catalyst (1.0 g), substrate (10 mmol), 1,2-dichloroethane (30 ml), and dinitrogen tetroxide (10 ml), were employed in a series of experiments in which the nitration of other aromatic compounds was attempted. The catalyst selected for use in these experiments was zeolite Hβ (Si/Al = 12.5). Out of all of the catalysts used in the experiments discussed in section 3.2.4, this catalyst was one of the catalysts that produced the best results for conversion, yield, and *para*-selectivity in the nitration of chlorobenzene under the given experimental conditions. It is for this reason that it was selected for use in these experiments as well.

In this series of experiments, the nitration of toluene, benzene, fluorobenzene, bromobenzene, and iodobenzene was attempted. The reaction times varied from 24 hours to 48 hours, and each reaction was conducted at 0 °C for the specified length of

time. The reaction products were analysed using gas chromatography. The reaction times and the results for each of these experiments are shown in Table 3.19.

After a relatively short reaction time, 24 hours, toluene had been completely consumed, with a percentage conversion of 100%. The yield of nitrotoluene was reasonable, at 85%.

Table 3.19. Reaction Times, Conversion, Yield, and Isomer Distributions when Different Aromatic Compounds are Nitrated Using Zeolite Hβ (Si/Al = 12.5) and Liquid Dinitrogen Tetroxide in 1,2-Dichloroethane Solvent.[a]

Substrate	**Time**	**Conversion[b]**	**Yield[b]**	**Isomer Distribution[b] (%)**		
Type	**(h)**	**(%)**	**(%)**	***ortho***	***meta***	***para***
Toluene	24	100	85	53	2	45
Benzene	45	55	50	-	-	-
Fluorobenzene	48	100	95	7	0	93
Chlorobenzene	48	98	95	14	<1	85
Bromobenzene	48	>99	94	22	<1	77
Iodobenzene	48	99	95	37	1	62

[a] All reactions were carried out with Hß zeolite (1.0 g), substrate (10.0 mmol), 1,2-dichloroethane (30 ml), and dinitrogen tetroxide (10 ml) at 0 °C. [b] Calculated by quantitative GC.

However, the *para*-selectivity of the reaction was fairly low, at 45%, although this level of selectivity for toluene nitration is still higher than that obtained when the mixed acid method is used for nitration.

Benzene gave only a modest yield of nitrated product under the current experimental conditions. At the end of 45 hours, only 55% of the benzene had been converted and the yield of nitrobenzene was 50%. Additional experiments may need to be performed to increase the conversion and yield of nitrobenzene. All of the halogenobenzenes used exhibited high levels of conversion, ranging from 98% to 100%. The yields were also good when the halogenobenzenes were used as the substrates in the reaction, with values around 94% to 95%. Only fluorobenzene produced very high levels of *para*-nitrated product, with a *para*-selectivity of 93%. The percentage of *para*-chloronitrobenzene produced was 85%, typical of the results seen in the other experiments in which chlorobenzene was the substrate. The *para*-selectivity of the reactions when bromobenzene and iodobenzene were nitrated was lower, at 77% and 62%, respectively. This decrease in the *para*-selectivity of the reaction was coupled with an increase in the level of *ortho*-substituted product. There appears to be a trend in the *para*-selectivity of these reactions, with benzene rings substituted with a more electronegative but smaller atom, *i.e.*, fluorine, producing the highest levels of *para*-nitrated product. As the electronegativity of the substituent attached to the benzene ring decreases, and the size and carbon-halogen bond length increase, there is a corresponding drop in the selectivity of the reaction and more *ortho*-substituted product is produced. These trends are matched in traditional nitration reactions.[9]

3.4 Conclusions

Most of the traditional methods of aromatic nitration reaction have relied on the use of dangerous chemicals and high temperatures to facilitate the nitration reaction, and the results obtained using these methods have, generally, been rather poor. A new method for nitrating aromatic compounds in an extremely efficient and cost-effective way has been developed. It offers significant advantages over the conventional mixed acid nitration methods and uses dinitrogen tetroxide as the nitrating reagent. The current method in which zeolite Hβ (Si/Al = 12.5) is used to catalyse the nitration reaction using dinitrogen tetroxide and 1,2-dichloroethane results in the *para*-selective production of a high yield of mono-nitrated products for most of the substrates used in these experiments. In addition, the reaction is simple and easy to use, and the catalyst can be recycled and reused many times. Lastly, the environmental concerns associated with the use of highly caustic compounds are eliminated when this method is used for the nitration of aromatic compounds.

3.5 References

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CHAPTER (4)

Nitration Using Zeolite Hß, Dinitrogen Tetroxide, and Air without Solvent

CHAPTER (4)

Nitration Using Zeolite Hβ, Dinitrogen Tetroxide, and Air without Solvent

4.0 Introduction

Historically, the nitration of aromatic compounds has been difficult, and the methods used to nitrate these compounds have been labour-intensive, time-consuming, and, generally, ineffective. A new method by which aromatic compounds could be nitrated using liquid dinitrogen tetroxide was presented in Chapter 3. Using this method, the nitration of several aromatic compounds was attempted, with varying degrees of success.

The method developed and discussed in Chapter 3 was shown to produce high levels of conversion and yield of nitrated aromatic compounds for most of the compounds used in the study. The exception to this statement was when benzene was used in the reaction, and, in fact, the lowest conversion and yield were produced when benzene was the reaction substrate. The *para*-selectivity for the nitration reaction varied, depending on the aromatic used in the reaction, with aromatics containing the most electronegative halogen substituent producing the highest level of *para*-nitrated product. The percentage of *para*-nitrated product decreased as the electronegativity of the ring substituent decreased.

Although this method was shown to produce significantly better results than most of the previously discussed nitration systems, there were still disadvantages associated with its use. For example, under the final set of reaction conditions

developed, *i.e.*, calcined zeolite Hβ (1.0 g), substrate (10 mmol), 1,2-dichloroethane (30 ml), and liquid dinitrogen tetroxide (10 ml), the reaction requires two days to go to completion. In addition, the reaction mixture has to be maintained at 0 °C. The reaction also requires the presence of a haloalkane solvent. And, while the reaction uses only 10 mmol of the aromatic compound, it requires about 163 mmol of nitrating reagent, a very high nitrating reagent to substrate ratio.

In an effort to modify the reaction conditions and eliminate some of these disadvantages, a new method by which aromatic compounds could be nitrated was investigated. The idea for this method was developed as a result of three different sets of experiments, all of which were performed in Prof. Keith Smith's laboratory at the University of Wales, Swansea, UK.

In the first study, completed by Simon Roberts, an autoclave was employed as a reactor for the regioselective alkylation of naphthalene.[1] The results of these experiments showed that an autoclave could be used with a high degree of success in alkylating naphthalene to produce the desired isomer. These results led to the idea that an autoclave may provide a suitable environment for the regioselective nitration of aromatic compounds. In another set of experiments, presented and discussed in Chapter 3, the feasibility of nitrating chlorobenzene in the absence of solvent was evaluated. The results of this experiment proved that solvent was not needed in order for the reaction to proceed, although the absence of solvent required an increase in the length of the reaction time if the reaction was to go to completion. Another series of experiments was completed in which the feasibility of using different amounts of dinitrogen tetroxide in the nitration of chlorobenzene was evaluated. These

experiments were also presented and discussed in Chapter 3. In this series of experiments, the amount of dinitrogen tetroxide used in the reaction did not affect the *para*-selectivity of the reaction. However, changing the amount of dinitrogen tetroxide used in the experiment did have an impact on the yield of chloronitrobenzenes.

Based on the results from these experiments, the current study in which the nitration of aromatic compounds using an autoclave in the absence of solvent and using reduced volumes of dinitrogen tetroxide was attempted. It was hoped that this new method would allow for the quick, efficient, and clean nitration of aromatic compounds.

4.1 Materials and methods

4.1.1 Chemicals and materials

The following aromatic compounds were used as substrates in the aromatic nitration reactions: benzene, toluene, fluorobenzene, chlorobenzene, bromobenzene, and iodobenzene. Information about these compounds, as well as about the standards used in gas chromatographic analysis was provided in Chapter 3.

Hexadecane was used as the internal standard in the gas chromatographic analysis. The purity of the hexadecane was 99%, and it was purchased from Aldrich.

Two solvents were used in these experiments. Dichloromethane was analytical grade and was purchased from Fisher. 1,2-Dichloroethane was HPLC grade and was purchased from Aldrich.

The aromatic compounds, standards, and solvents were used as they were received. No additional processes were performed on them to render them suitable for use in these experiments.

Nitrogen dioxide gas was purchased from BOC Gases (EEC No. 2341264) and was used to prepare liquid dinitrogen tetroxide, the nitrating reagent in each experiment. The liquid dinitrogen tetroxide was prepared as described in Chapter 3. The oxygen, nitrogen, and air gases were purchased from BOC Gases.

Several different catalysts were used in the development of this method. Zeolites NH_4ß, Naß, HZSM-5 (50, 150, 1000 ratios), and NaY were gifts from Zeolyst International, and zeolite Hβ was prepared from zeolite NH_4β by calcining zeolite NH_4β at 550 °C for 24 hours. Zeolite NH_4-mordenite and NH_4Y were also from Zeolyst International and were used to prepare the H mordenite and HY catalyst via calcination.

Zeolites Liß, Mgß, Feß, Znß and Csß zeolites were prepared by Adam Musson in 1996.[2]

The reaction vessel for these experiments was a 450 ml autoclave from Parr Instrument Company, USA.

The reaction components were placed in a removable, open top, cylindrical liner composed of poly(ethyleneterephthalate) PTEF inside the autoclave and were retained there for the duration of the reaction.

Sodium hydroxide volumetric standard with a concentration of 0.1 M was used in the titration of nitric acid and was obtained from Aldrich. Phenolphthalein, also used in the titration analysis, was obtained from Aldrich.

4.1.2 Nitration of aromatic compounds

The basic procedure for each of the nitration reactions was the same, with only the variable being examined in a given study changing from experiment to experiment. Generally, calcined zeolite and the substrate were placed into the reaction vessel. In the experiments in which solvent was used, solvent was also added to the reaction vessel. Liquid dinitrogen tetroxide was quickly added to the reaction mixture and the autoclave was sealed and connected to a gas cylinder. The interior of the autoclave was pressurised to the desired pressure, then the gas was disconnected from the autoclave, leaving the pressurised gas in the autoclave for the duration of the reaction. The reaction was allowed to continue for a specified length of time with stirring.

Upon completion of the reaction time, the autoclave was opened and the product was extracted with either dichloromethane or 1,2-dichloroethane. Dichloromethane was used in all experiments in which 1,2-dichloroethane solvent was not used as part of the reaction mixture. 1,2-Dichloroethane was used to extract the reaction products in the few experiments in which it was used as the solvent in the reaction. The mixture was filtered and the zeolite washed with 100 ml of either dichloromethane or 1,2-dichloroethane. The filtrate was washed with water and dried over $MgSO_4$, concentrated under reduced pressure, and analysed using gas chromatography as described in Chapter 3, using hexadecane as the internal standard.

4.2 Nitration of chlorobenzene using an autoclave

As in the previous study, chlorobenzene was the first compound upon which nitration was attempted. There were several experimental parameters that needed to be evaluated if chlorobenzene was to be nitrated effectively, and the goal of the first part of this study was to determine the best conditions under which chlorobenzene could be nitrated by experimentally examining each of the parameters. These parameters included how temperature affected the reaction; whether or not solvent was required for the reaction; how the pressure of oxygen, nitrogen or air gases affected the conversion, yield, and *para*-selectivity of the reaction; which catalyst produced the best results; and the amount of nitrating reagent required for the reaction.

Studies were performed to establish the best parameters under which the nitration could occur. The results of these studies are presented in the following sections.

4.2.1 Temperature and solvent effects on the nitration of chlorobenzene

In the previous study in which aromatic compounds were nitrated using zeolite Hβ catalyst with dinitrogen tetroxide in the presence of oxygen, the nitration reaction had been conducted at 0 °C. Although the results of that study were very positive, one of the goals of this study was to improve upon that method, and, hopefully, eliminate or reduce some of the difficulties associated with its use.

Maintaining the temperature of the reaction system at 0 °C for 48 hours was one of the difficulties associated with the use of this method, and it was thought that it might be possible to increase the temperature at which the nitration reaction occurred

when using the autoclave system. For this reason, the effect of temperature on the nitration reaction was the first aspect of the experimental system to be studied.

The evaluation of the effects of temperature on the nitration reaction was separated into two distinct phases. In the first phase, calcined zeolite Hβ (1.0 g, SiO_2/Al_2O_3 = 25), chlorobenzene (10 mmol), liquid dinitrogen tetroxide (10 ml), and 1,2-dichloroethane (30 ml) were used as the catalyst, substrate, nitrating reagent, and solvent, respectively. Oxygen gas was used in this reaction at a pressure of 100 psi, a pressure that was arbitrarily selected. The reaction temperatures and times were varied, and the products of the reaction were analysed using gas chromatography. The results of these experiments are presented in Table 4.1.

In these experiments, two reaction temperatures were used, 40 °C and 60 °C. The reaction times for these experiments were 20 minutes and 60 minutes, respectively. Interestingly, increasing the temperature from 0 °C resulted in 100% conversion of chlorobenzene to chloronitrobenzene under both of the experimental conditions examined.

Table 4.1. The Conversion, Yield, and Isomer Distributions of Chloronitrobenzene Formed When 30 ml 1,2-Dichloroethane Solvent is Present in the Reaction mixture.

Temp.	**Time**	**Conversion[b]**	**Yield[b]**	**Isomer Distribution[b] (%)**		
(°C)	**(Min.)**	**(%)**	**(%)**	***ortho***	***meta***	***para***
40	20	100	96	19	<1	81
60	60	100	97[a]	9	<1	82

[a] Includes 9% 2,4-dinitrochlorobenzene formed during the course of this reaction. [b] Calculated by quantitative GC.

In addition, the *para*-selectivity of the reaction was maintained, with 81-82% *para*-chloronitrobenzene produced. However, unlike in the other experiments, in which only mononitrated products were produced during the reaction, the nitration of chlorobenzene at 60 °C for 60 minutes also produced 9% of 2,4-dinitrochlorobenzene, an undesirable reaction product.

Based on these results, the next phase of the study was begun. In this phase, the reaction was examined, again using two temperatures, but, in these experiments, no solvent was used. The same amounts of catalyst, substrate, and nitrating reagent were employed in the reaction, the oxygen pressure was maintained at 100 psi, and the reaction products were analysed using gas chromatography. The results of these experiments are shown in Table 4.2.

Table 4.2. The Conversion, Yield, and Isomer Distributions of Chloronitrobenzene Formed in the Absence of Solvent at Varions Reaction Times and Temperatures.[a]

Temp.	**Time**	**Conversion[b]**	**Yield[b]**	**Isomer Distribution[b] (%)**		
(°C)	**(Min.)**	**(%)**	**(%)**	***ortho***	***meta***	***para***
25	5	67	42	15	<1	85
25	45	100	93	17	<1	83
60	1	100	97	16	<1	84

[a] All reactions were carried out with chlorobenzene (10.0 mmol), zeolite Hß (1.0 g), and dinitrogen tetroxide (10 ml). [b] Calculated by quantitative GC.

In the first experiment attempted in the absence of solvent, the reaction temperature was 25 °C and the reaction time was 5 minutes. However, under these conditions, only 67% of the chlorobenzene was converted to products. The yield was

also low, 42%, although, not unexpectedly, the *para*-selectivity of the reaction was 85%, a value consistent with results obtained previously. From these results, it was clear that the reaction could proceed at room temperature, but it was suspected that the reaction time would require lengthening if the reaction was to proceed to completion. For this reason, the next experiment in this series maintained the same reaction temperature, but the reaction was allowed to continue for 45 minutes. At the end of this reaction time, 100% of the chlorobenzene had been converted to products, with a yield of 93%. The *para*-selectivity of this reaction was 83%.

Lastly, the aromatic nitration reaction was attempted at 60 °C, again in the absence of solvent. Because 2,4-dinitrochlorobenzene was produced when this reaction had been attempted previously at 60 °C with a 60 minute reaction time, the reaction time for this experiment was decreased to 1 minute. Amazingly, the conversion at the end of this reaction time was 100%. As when the reaction temperature was 25 °C with a reaction time of 45 minutes, the yield of chloronitrobenzene was 97%. The *para*-chloronitrobenzene produced was 84%, and no 2,4-dinitrochlorobenzene was produced.

From these experiments, three important aspects of this new nitration system were established. First, it was possible to increase the reaction temperature to room temperature, thus eliminating the need to maintain the reaction at low temperatures during the course of the reaction. Second, unlike in the previous system, the use of solvent in the reaction mixture could be eliminated without causing adverse effects on the progression of the reaction. Third, the reaction time was drastically reduced when the autoclave was used as the reactor in which the nitration reaction occurred. These

results were incorporated into subsequent experiments, with later experiments taking place at room temperature and in the absence of solvent, and a series of experiments being completed in which the effect of time on the nitration reaction was evaluated.

4.2.2 Use of gases

4.2.2.1 Use of oxygen gas

Many chemical reactions require an oxidation reagent. In the previous study presented in Chapter 3, the oxidation reagent, oxygen gas, was supplied to the reaction mixture by flushing the reaction mixture for 20 minutes. Additionally, oxygen was continually supplied to the reaction mixture during the entire course of the reaction. In section 4.2.1, the effects of temperature and solvent on the nitration reaction were evaluated, and oxygen gas was added to the autoclave to a pressure of 100 psi. Once the desired pressure had been reached, the autoclave was disconnected from the oxygen source and the oxygen sealed inside the reactor for the duration of the reaction time. The results of these experiments showed that nitration of chlorobenzene was possible under these reaction conditions, however, the pressure of oxygen applied to the system was selected arbitrarily. Until this time, no scientific studies had been pursued in an effort to determine the pressure of oxygen needed in order for the nitration reaction to proceed.

A series of experiments in which various pressures of oxygen gas were applied to the autoclave was begun, with the purpose of determining the pressure of oxygen gas needed in order to facilitate the nitration of chlorobenzene in a timely and efficient manner. In this series of experiments, calcined zeolite Hβ (1.0 g,

SiO_2/Al_2O_3 = 25), chlorobenzene (10 mmol), and dinitrogen tetroxide (10 ml) were added to the autoclave and varying pressures of oxygen gas were applied to the system. The reaction time for each experiment was 20 minutes, and the experiments were conducted at room temperature (25 °C). The products of the reaction were analysed using gas chromatography, and the results of these experiments are presented in Table 4.3.

In the first experiment in this series, no oxygen gas was added to the autoclave. The purpose of this experiment was to determine whether or not the reaction would proceed under air, charged at atmospheric pressure.

Table 4.3. The Conversion, Yield, and Isomer Distributions of Chloronitrobenzene Formed under Various Pressures of Oxygen Gas for 20 Minutes.[a]

Oxygen	**Conversion** [b]	**Yield** [b]	**Isomer Distribution** [b] **(%)**		
(psi)	**(%)**	**(%)**	***ortho***	***meta***	***para***
-	4	1	14	0	86
100	55	47	14	<1	85
80	52	47	14	<1	85
70	43	37	14	0	86
50	32	26	14	0	86

[a] All reactions were carried out with chlorobenzene (10.0 mmol), zeolite Hß (1.0 g), and dinitrogen tetroxide (10 ml) at 25 °C for 20 minutes. [b] Calculated by quantitative GC.

The conversion of chlorobenzene into products in this experiment was only 4%, with a yield of 1%. In the second experiment, 100 psi of oxygen gas was used.

The conversion in this experiment was 55% with yield of 47%. Although the conversion and yield were only about half the level of conversion and yield obtained in the experiments discussed in section 4.2.1, the reaction time in this experiment was only 20 minutes, compared to 45 minutes in the first set of experiments. The next experiment utilised 80 psi oxygen, with approximately the same results obtained as when 100 psi oxygen was used. When 80 psi oxygen was used, the conversion was 52% and the yield was 47%. As the pressure of oxygen was further decreased to 70 and 50, the level of conversion also decreased to values of 43% and 32%, respectively. As expected, the yield of chloronitrobenzene also decreased, producing values of 37% when 70 psi oxygen was used and 26% when 50 psi oxygen was used. The *para*-selectivity of the reaction was approximately the same, regardless of the pressure of oxygen present in the system, at 85%-86%.

Based on the results of these experiments, 100 psi oxygen produces the highest levels of conversion and yield when nitrating chlorobenzene, without sacrificing the *para*-selectivity of the reaction, and this pressure was selected for use in subsequent experiments.

4.2.2.2 Use of nitrogen gas

Although the use of oxygen in this experiment produced favorable results, it was unknown whether or not oxygen was actually required for the reaction. The possibility existed that the nitration of chlorobenzene in this system was not dependent on the presence of oxygen. Rather, the possibility existed that the nitration was proceeding in response to the increased pressure on the reaction mixture. For

this reason, another experiment was attempted in which 200 psi of nitrogen gas was placed into the autoclave unit. As in the experiments in which oxygen gas was used, the reaction mixture was composed of zeolite Hβ (1.0 g, SiO_2/Al_2O_3 = 25), chlorobenzene (10 mmol), and dinitrogen tetroxide (10 ml). The reaction time and temperature also remained the same, at 20 minutes and room temperature, respectively, and the reaction products were analysed using gas chromatography.

However, when nitrogen gas was used under these reaction conditions, only 1% of the chlorobenzene originally present in the reaction mixture was consumed, and the yield of chloronitrobenzene was unmeasurably small. Therefore, the conclusion is that the reaction is not occurring as a result of the pressure applied to the reaction mixture, rather, the presence of oxygen as an oxidation agent is required for the reaction to take place.

4.2.2.3 Use of air

As shown in Table 4.2, 100% conversion of chlorobenzene to products was obtained when oxygen was used as the oxidation reagent in the autoclave system at a pressure of 100 psi at room temperature. In addition, the yield of chloronitrobenzene under these conditions was 93% and the *para*-selectivity of the reaction was 83%. These results, coupled with the results obtained when various pressures of oxygen gas were used, indicated that oxygen gas was a good choice for use as the oxidation reagent in future experiments.

For this reason, oxygen gas was used in several subsequent studies and data were obtained from these experiments. However, oxygen gas enhances the

possibility of explosion and, actually, there were several small explosions in the laboratory when oxygen gas was used while this method was under development. Because of the safety issues surrounding the use of oxygen gas in this study, a feasibility study was begun in which air was used as the oxidation reagent. It was thought that, although the percentage of oxygen in air was only about one fifth of that found in pure oxygen gas, air might contain a concentration of oxygen high enough to allow the reaction to proceed. At the same time, using air instead of oxygen gas would allow the reaction to proceed under much safer conditions and would be cheaper.

In this study, calcined zeolite Hβ (1.0 g, SiO_2/Al_2O_3 = 25), 10 mmol of chlorobenzene, and dinitrogen tetroxide (10 ml) were reacted in an autoclave to which various pressures of air had been applied. The reaction proceeded at room temperature (25 °C) for 30 minutes, then the reaction products were analysed using gas chromatography. The results of this series of experiments are shown in Table 4.4.

In these experiments, the air pressure was varied from a low value of 100 psi to a high value of 250 psi. The results obtained when 100 psi of air was used in the reaction showed only a 50% conversion with 44% yield of chloronitrobenzenes. These results were very close to the results obtained when 100 psi of oxygen was used in the reaction with a reaction time of 20 minutes, although the reaction time was increased in the current study to compensate for the reduced amount of oxygen present in the sample of air.

Table 4.4. The Conversion, Yield, and Isomer Distributions of Chloronitrobenzene Formed under Various Pressures of Air for 30 Minutes.[a]

Air (psi)	Conversion[b] (%)	Yield[b] (%)	Isomer Distribution[b] (%)		
			ortho	*meta*	*para*
100	50	44	14	0	86
150	61	56	14	0	86
200	70	60	15	0	85
250	70	61	15	0	85

[a] All reactions were carried out with chlorobenzene (10.0 mmol), zeolite Hß (1.0 g), and dinitrogen tetroxide (10 ml) at 25 °C for 30 minutes. [b] Calculated by quantitative GC.

As the amount of air in the autoclave increased, so did the conversion and yield. When 150 psi of air was used, the conversion increased to 61%, with a 56% yield, an 11% increase in conversion and 12% increase in yield over the results obtained when 100 psi of air was used. When the amount of air in the autoclave was increased to 200 psi, the conversion was 70% and yield was 60%. Almost the same results were obtained when the amount of air was increased to 250 psi, with a conversion level of 70% and yield of 61%, indicating that additional increases in the amount of air present in the system did not correlate with increased conversion and yield. The *para*-selectivity of the reaction, at 85-86%, was virtually the same for all of the reactions, regardless of the amount of air in the system.

Based on the results of this study, 200 psi of air was used in the studies undertaken in which air was used as the oxidation reagent.

4.2.3 Effects of zeolite on the nitration of chlorobenzene

Another important aspect in the development of this nitration method was to determine the best catalyst for use in this method. Zeolite Hβ (Si/Al = 12.5) had been used very successfully in earlier experiments in this study, as well as in the development of the method discussed in Chapter 3. However, it was unknown whether another type of catalyst may provide better results.

A series of experiments was begun in which a consistent quantity (1.0 g) of different catalysts was used in the nitration reaction. The catalysts selected for use in these experiments differed in their structural characteristics, as well as in their silicon to aluminium ratios. The zeolite β and Y families are large pore catalysts, with silicon to aluminium ratios ranging from 12 to 30. H mordenite has a linear structure with a silicon to aluminium ratio of 10.5. The two HZSM-5 catalysts used in these experiments are medium pore catalysts with silicon to aluminium ratios of either 50 or 150.

The catalyst was used for reactions of chlorobenzene (10 mmol) with dinitrogen tetroxide (10 ml) under 100 psi of oxygen at room temperature. The reaction time was varied between 30 minutes and 1 hour. As in the other experiments, the reaction products were analysed using gas chromatography. The types of zeolites used in these reactions, as well as their silicon to aluminium ratios, reaction times, and the results for these experiments are shown in Table 4.5.

Not surprisingly, the use of zeolites Hβ and HY as the reaction catalysts resulted in the highest conversions and yields of chloronitrobenzenes. When zeolite Hβ was used in the reaction, the conversion was 99% and the yield was 95%. Use of

zeolite HY in the reaction produced a conversion of 99% and a yield of 96%. Although these values for conversion and yield are very close to one another, the reaction was not as selective when zeolite HY was used. When zeolite HY was used in the reaction, the *para*-selectivity was 80%.

Table 4.5. The Conversion, Yield, and Isomer Distributions of Chloronitrobenzene Formed Using Different Catalysts.[a]

Zeolite	**Si/Al**	**Time**	**Conversion[b]**	**Yield[b]**	**Isomer Distribution[b] (%)**		
	Ratio	**(Min.)**	**(%)**	**(%)**	***ortho***	***meta***	***para***
Hß	12.5	30	99	95	15	<1	84
Naß	12	30	76	70	17	0	83
HY	30	40	99	96	19	<1	80
NaY	28	40	81	75	19	<1	80
H-Mord.	10.5	60	43	30	30	0	70
HZSM-5	50	60	43	35	26	0	74
HZSM-5	150	60	34	26	16	0	84

[a] All reactions were carried out with chlorobenzene (10.0 mmol), zeolite Hß (1.0 g), dinitrogen tetroxide (10 ml), and 100 psi oxygen at 25 °C. [b] Calculated by quantitative GC.

In contrast, zeolite Hβ produced 84% *para*-chloronitrobenzene when it was used in the reaction, a value more typical of the results obtained in previous experiments.

None of the other catalysts used in these experiments produced satisfactory results. The conversions ranged from 34% to 81%, with yields ranging from 26% to

75%. Even the selectivity of the reaction, which had been shown in most previous experiments to stay at a reasonably constant level, decreased when most of these other catalysts were used, with values ranging from 70% to 80%, except when HZSM-5 (Si/Al = 150) was used. When HZSM-5 (Si/Al = 150) was used in the reaction, the *para*-selectivity of the reaction was higher, with a value of 84%, similar to that with Hß. However, the use of this catalyst resulted in the lowest conversion and yield. Unfortunately, the selectivity of the reaction cannot compensate for the decrease in the level of conversion and yield of chloronitrobenzene. Thus, this catalyst, although it maintains the same degree of *para*-selectivity as zeolite Hβ, is not a suitable catalyst for use in this system.

Although many different catalysts were studied and their abilities to nitrate aromatic compounds effectively were evaluated, only one catalyst, zeolite Hβ, was found to produce high conversions and yields of chloronitrobenzenes while still maintaining the *para*-selectivity of the reaction. For this reason, zeolite Hβ was used in subsequent experiments in the development of this method.

4.2.4 Effects of using different volumes of dinitrogen tetroxide on the nitration of chlorobenzene

Another aspect of the experimental system that needed to be optimised while developing this method was the volume of dinitrogen tetroxide used in the experiment.

In this work, different volumes of dinitrogen tetroxide were reacted with zeolite Hβ (3.0 g) and chlorobenzene (33 mmol) under 200 psi of air at room

temperature. The volumes of dinitrogen tetroxide used, the reaction time for each experiment, and the results of these experiments are shown in Table 4.6.

The goal of this series of experiments was to determine the minimum amount of dinitrogen tetroxide needed to cause 100% conversion of chlorobenzene to products.

Table 4.6. The Conversion, Yield, and Isomer Distributions of Chloronitrobenzene Produced Using Different Volumes of Dinitrogen Tetroxide.[a]

N_2O_4 (ml)	Time (h)	Conversion [b] (%)	Yield [b] (%)	Isomer Distribution [b] (%)		
				ortho	*meta*	*para*
0.5	46	41	33	14	<1	85
1.0	46	74	69	16	<1	84
1.0	168	75	73	15	<1	85
1.4	46	100	96	15	<1	84
2.0	46	100	92	19	<1	81

[a] All reactions were carried out with chlorobenzene (33 mmol), zeolite Hß (3.0 g), and 200 psi air at 25 °C. [b] Calculated by quantitative GC.

In the first experiment, the volume of dinitrogen tetroxide used was 0.5 ml, and the results of this experiment showed that 41% of the chlorobenzene was consumed to give a 33% yield of chloronitrobenzene at the end of the 46 hours reaction time. When the volume of dinitrogen tetroxide was increased to 1 ml and the reaction time was 46 hours, the conversion increased to 74%, with a yield of 69%. After this experiment was complete, another experiment was performed in which the reaction time was increased to 168 hours while the volume of dinitrogen tetroxide

used remained at 1 ml. In this experiment, the yield increased from 69% to 73%, however, the conversion increased by only one percent, to 75%. The lack of substantial increase in the conversion as the reaction time for the experiment was lengthened indicated that all of the dinitrogen tetroxide present in the system had reacted with the chlorobenzene in the system. Thus, the chlorobenzene substrate was still present in excess in the reaction mixture by 25%. Theoretically, increasing the amount of dinitrogen tetroxide used in the reaction by at least 33% should lead to 100% conversion of chlorobenzene to chloronitrobenzene. This hypothesis was shown to be true. When the volume of dinitrogen tetroxide was increased to 1.4 ml, the conversion of chlorobenzene to products was 100% when the reaction time was 46 hours. In this reaction, the dinitrogen tetroxide was present in a slight excess (about 23 mmol, *i.e.* 46 mmol of NO_2, a 25% excess over the 33 mmol of chlorobenzene used). The last experiment in this series employed dinitrogen tetroxide in a volume of 2 ml, or about 33 mmol. In this experiment, the conversion of the chlorobenzene to chloronitrobenzen was 100% with 92% yield. However, unlike in the previous experiments, in which the *para*-selectivity of the reaction was consistent at 84%-85%, there was a slight decrease in the *para*-selectivity of the reaction, to 81%.

There are many advantageous aspects of the results of the current study. Unlike in the previous experiments, where about 163 mmol (10 ml) of dinitrogen tetroxide was used as the nitrating reagent, the amount of nitrating reagent needed for the nitration reaction to proceed to completion has been radically reduced to 23 mmol (1.4 ml). At the same time, the amount of substrate used in the reaction has been

increased to three times the level of substrate used in previous reactions, while still maintaining high levels of conversion, yield, and *para*-selectivity, leading to an increase in the amount of chloronitrobenzene produced from each experiment. Based on the results of these experiments, these new reaction conditions in which zeolite Hβ (3.0 g), chlorobenzene (33 mmol), and liquid dinitrogen tetroxide (1.4 ml, 23 mmol) are reacted under 200 psi of air were used to evaluate several additional experimental parameters.

4.2.4.1 Effects of reaction time on the nitration of chlorobenzene using reduced volumes of dinitrogen tetroxide

Until now, only a very rough preliminary estimate of the amount of time needed for the nitration of chlorobenzene using this system had been determined. The results of these experiments had shown that the conversion of chlorobenzene to products was only 67% at room temperature when the reaction time was five minutes. The conversion was increased to 100% when the reaction time was 45 minutes. In that experiment, 100 psi of oxygen gas was used as the oxidising reagent and the amount of dinitrogen tetroxide used was about 163 mmol, with zeolite Hβ (1.0 g) and chlorobenzene (10 mmol). If these were still the conditions under which the experiment was being conducted, then it would be reasonable to begin a formal study of the reaction times by increasing the reaction times from 5 minutes to 45 minutes in small increments. The reaction would proceed for the specified length of time, then the reaction products would be analysed. Thus, the progression of the reaction could be monitored.

However, the results of subsequent experiments have indicated that the original parameters upon which this method was based were not the best parameters for use in this method, and all of the original parameters upon which this study had been based have been changed. In the current experiments, catalyst (3.0 g), chlorobenzene (33 mmol), dinitrogen tetroxide (1.4 ml, 23 mmol) and 200 psi of air are used. Because of these changes, the results obtained in the previous experiment in which the reaction times were monitored may no longer be valid. For this reason, it was important to complete a formal study to determine the reaction time needed to produce the highest level of conversion, yield, and *para*-selectivity of the reaction.

In this series of experiments, reaction times varying from 1.5 hours to 14 hours were used, and the reaction products analysed using gas chromatography. The reaction times and the results of these experiments are shown in Table 4.7.

In the previous experiments presented in section 4.2.1, the conversion of chlorobenzene was 100% when the reaction time was 45 minutes. However, in the experiments in the current study, the amount of dinitrogen tetroxide was decreased, while the amount of substrate used in the experiment was increased.

Results from experiments in Chapter 3, in which the volume of dinitrogen tetroxide was decreased from 10 ml to 5 ml showed that a significant increase in the reaction time was needed if a high level of conversion of chlorobenzene to products was to be obtained. Based on this information, the first reaction time used in these experiments was 1.5 hours, twice as long as the reaction time used in which 100% conversion was obtained when a higher volume of dinitrogen tetroxide was used.

Table 4.7. The Conversion, Yield, and Isomer Distributions of Chloronitrobenzene Produced when the Reaction Time Varies. [a]

Time (h)	Conversion [b] (%)	Yield [b] (%)	Isomer Distribution [b] (%)		
			ortho	*meta*	*para*
1.5	25	18	19	<1	80
3.5	50	40	18	<1	81
6	69	63	19	<1	80
9.5	87	81	17	<1	82
14	100	97	15	<1	84

[a] All reactions were carried out with chlorobenzene (33 mmol), zeolite Hß (3.0 g), dinitrogen tetroxide (1.4 ml, 23 mmol), and air (200 psi) at 25 °C. [b] Calculated by quantitative GC.

The results of this experiment showed that only 25% of the chlorobenzene originally in the system was consumed, with 18% yield of chloronitrobenzenes, and 80% *para*-selectivity for the reaction. As the reaction time was increased to 3.5 hours, the conversion was doubled, to 50%, and the yield was increased by 22%, to 40%, with *para*-selectivity of 81%. The next reaction time, 6 hours, resulted in the conversion of 69%, with a yield of 63% and *para*-selectivity of 80%. Further increase in the length of the reaction time to 9.5 hours and 14 hours resulted in conversions of 87% and 100%, respectively, with yields of 81% and 97%. In addition, the *para*-selectivity of the reaction continued to increase, with 82% *para*-selectivity when the reaction time was 9.5 hours, and 84% *para*-selectivity when the reaction time was 14 hours.

From these results, it is clear that altering the levels of nitrating reagent, catalyst, and substrate in the reaction radically alters the rate of the nitration reaction

at room temperature. When the substrate to nitrating reagent ratio is 1:16 the reaction proceeds very quickly, with a reaction time of 45 minutes and conversion of 100%. However, when the substrate to nitrating reagent ratio is altered to 1:1.4 the reaction proceeds at a much slower rate, but the conversion is still 100% at the end of 14 hours reaction time. Although the rate of the reaction is much slower, the amount of nitrating reagent used in the reaction mixture is much more reasonable, leading to less waste of materials and greater efficiency. For this reason, a reaction time of 14 hours along with 1.4 ml of dinitrogen tetroxide was selected for use in subsequent experiments in which the nitration of chlorobenzene was attempted.

4.2.4.2 Effects of zeolite on the nitration of chlorobenzene using reduced volumes of dinitrogen tetroxide

The effects of using different types of zeolite catalysts in the nitration of chlorobenzene had been evaluated using the original experimental parameters of zeolite Hβ (1.0 g), chlorobenzene (10 mmol), and dinitrogen tetroxide (10 ml, *ca.* 163 mmol). Although the previous study had shown that using zeolite Hβ provided the best levels of conversion, yield, and *para*-selectivity of the nitration reaction, it was unknown whether these results would be maintained when the ratio of catalyst to substrate to nitrating reagent was altered.

For this reason, another study was completed in which the effects of different catalysts on the nitration reaction using the reduced substrate to nitrating reagent ratio of 1:1.4 were examined, using zeolite (3.0 g), chlorobenzene (3.35 ml, 33 mmol), and liquid dinitrogen tetroxide (1.4 ml, *ca.* 23 mmol) under 200 psi air. The same

catalysts used in section 4.2.3 were used in this series of experiments. The effects of one additional catalyst, HZSM-5 with a silicon to aluminium ratio of 1000, were also evaluated, as was the progression of the reaction in the absence of any catalyst. Although experiments had been conducted in which the best reaction time had been determined using zeolite Hβ as the reaction catalyst, preliminary studies with other catalysts indicated that 14 hours was not a sufficient reaction time for many of these reactions. For this reason and to better evaluate the effects of the catalysts used in these experiments on the conversion, yield, and *para*-selectivity of the nitration reaction, the reaction times in these experiments were varied. The reaction times and the results of the experiments are shown in Table 4.8.

Out of all of the catalysts evaluated in this series of experiments, zeolite Hβ produced the best results, with 100% conversion, 97% yield, and 84% *para*-selectivity using the shortest reaction time. None of the other catalysts used in this experiment produced results comparable to those obtained when zeolite Hβ was used as the catalyst in the reaction, even when the reaction times were increased, with conversion values ranging from 70-89%. There was also a large fluctuation in the yield of chloronitrobenzene in these experiments. And, when zeolites other than Hβ and Naβ were used, the *para*-selectivity of the reaction decreased to less than 80%.

Interestingly, the *para*-selectivity of the reaction was essentially the same as the *para*-selectivity of the reaction presented in section 4.2.3 for some of the catalysts used, such as Hβ, Naβ, H mordenite, and HZSM-5 (Si/Al = 50). The use of other catalysts, such as HY, NaY, and HZSM-5 (Si/Al = 150), resulted in a significant

decrease in the level of *para*-selectivity of the reaction when compared to the results presented in the same section.

Table 4.8. The Reaction Time, Conversion, Yield, and Isomer Distributions of Chloronitrobenzenes Formed Using Different Zeolites and 1.4 ml Liquid Dinitrogen Tetroxide under Air 200 psi.[a]

Zeolite	**Si/Al**	**Time**	**Conversion**[b]	**Yield**[b]	**Isomer Distribution**[b] (%)		
Type	**Ratio**	**(h)**	**(%)**	**(%)**	***ortho***	***meta***	***para***
None	-	24	38	34	34	<1	65
Hß	25	14	100	97	15	<1	84
Naß	24	24	90	80	19	<1	80
HY	30	24	80	75	27	<1	72
NaY	28	21	76	68	25	<1	74
H-Mord.	10.5	24	81	70	29	1	70
HZSM-5	50	24	86	82	26	1	74
HZSM-5	150	24	89	78	24	<1	76
HZSM-5	1000	24	70	54	27	<1	72

[a] All reactions were carried out with chlorobenzene (33 mmol), zeolite (3.0 g), dinitrogen tetroxide (1.4 ml, 23 mmol), and air (200 psi) at 25 °C. [b] Calculated by quantitative GC.

However, the differences in the selectivity of the reaction when zeolites HY and NaY are used could be related to the response of the catalyst structure to the pressure in the system, which had been increased from 100 psi to 200 psi. It is possible that the change in pressure could produce a change in the ring-like structure of the zeolites HY and NaY, resulting in a structure that is less capable of producing

selectively nitrated chlorobenzene. The decrease in the level of selectivity for *para*-nitrated chlorobenzene when HZSM-5 (Si/Al = 150) was used as the catalyst is more difficult to explain, although it could be related to the differing silicon to aluminium ratio. How the silicon to aluminium ratio of the catalyst may affect the reaction is unknown, especially considering that the level of selectivity of the reaction was not decreased when HZSM-5 (Si/Al = 50) was used as the catalyst instead of HZSM-5 (Si/Al = 150).

From these experiments, it is clear that zeolite Hβ retains its ability to nitrate chlorobenzene efficiently, even under the new reaction conditions, using decreased dinitrogen tetroxide and increased amounts of catalyst, substrate, and air pressure. Unfortunately, acceptable levels of nitration and regioselectivity of the nitration reaction were not obtained when other catalysts were used in the reaction, even when the reaction time was increased. Because of its demonstrated ability to catalyse the nitration reaction effectively, zeolite Hβ was selected for use in the nitration of other aromatic compounds.

4.2.4.2.1 Effects of the presence of different counter-cations in zeolite β on the nitration of chlorobenzene

One of the interesting results of the previous series of experiments was that zeolites Hβ and Naβ retained their ability to nitrate chlorobenzene selectively at the *para*-position, even though there were several aspects of the experimental conditions that had changed. This ability was not maintained by most of the other catalysts used,

notably HY and NaY, two catalysts which had produced good results when used for the nitration reactions presented in section 4.2.3.

Although the results obtained when zeolites Hβ and Naβ were used in the experiments presented in section 4.2.4.2 showed that both of these catalysts could effectively catalyse the nitration reaction, zeolite Hβ was a better catalyst for the reaction than zeolite Naβ. The silicon to aluminium ratio in these two catalysts was almost the same, 12.5 for zeolite Hβ and 12 for zeolite Naβ. The only other difference between these two catalysts was the type of counter-cation in the zeolite. To evaluate the effects of the cation on the ability of zeolite β to catalyse the *para*-selective nitration of chlorobenzene, a series of experiments as completed in which several different types of zeolite β, each with a different cation, were used as the reaction catalyst. The silicon to aluminium ratios of each catalyst, the reaction time used in each experiment, and the amounts of catalyst, chlorobenzene, and dinitrogen tetroxide used in each experiment are shown in Table 4.9.

The results from these experiments, as well as previous results when zeolites Hβ and Naβ were used, are shown in Table 4.10.

In past experiments when hydrogen has been used as the cation in zeolite β, it has consistently given high rates of conversion, yield, and *para*-selectivity of the nitration reaction.

Of all of the cations, hydrogen has the smallest size, and its use as the reaction catalyst results in the production of the highest amount of *para*-chloronitrobenzene. As shown in Table 4.10, as the size of the cation in the zeolite increased, the

effectiveness of the zeolite to catalyse the *para*-selective nitration of chlorobenzene decreased.

Table 4.9. Types of Cations used in Zeolite β, Reaction Time, and Amounts of Catalyst, Chlorobenzene and Dinitrogen Tetroxide used in each Reaction.[a]

Cation Type	**Time (h)**	**Zeolite β (g)**	**Chlorobenzene (mmol)**	**N_2O_4 Volume (ml)**
H	14	3.0	33	1.4
Li	24	1.5	16	0.70
Na[b]	24	3.0	33	1.4
Mg	24	1.5	16	0.70
Fe	24	1.5	16	0.70
Zn	24	1.5	16	0.70
Cs	24	1.5	16	0.70
NH_4	24	3.0	33	1.4

[a] The SiO_2/Al_2O_3 ratio of catalysts was 25. [b] SiO_2/Al_2O_3 ratio was 24.

Evidence of this trend is apparent, with zeolite Liβ, the zeolite with the next smallest cation, producing the second highest amount of *para*-chloronitrobenzene and zeolite Csβ, the zeolite with the largest cation, producing the least amount of *para*-chloronitrobenzene.

These changes in the *para*-selective nitration of chlorobenzene could be the result of the decreased pore size of the zeolite, resulting from the presence of larger cations within the zeolite pores.

Table 4.10. The Conversion, Yield, and Isomer Distributions of Chloronitrobenzene Formed when Zeolite ß with Different Cations is Used as Reaction Catalyst.[a]

Cation Type	Conversion[c] (%)	Yield[c] (%)	Isomer Distribution[c] (%)		
			ortho	*meta*	*para*
H	100	97	15	<1	84
Li	95	91	17	<1	82
Na[b]	90	80	19	1	80
Mg	80	72	21	<1	79
Fe	94	88	21	<1	79
Zn	91	83	19	<1	80
Cs	78	61	31	<1	69
NH_4	58	44	24	<1	75

[a] The SiO_2/Al_2O_3 ratio of catalysts was 25. [b] The SiO_2/Al_2O_3 ratio was 24.
[c] Calculated by quantitative GC.

4.3 Nitration of aromatic compounds using optimised nitration conditions

At this point, several aspects of the experimental system have been optimised in order to allow chlorobenzene to be nitrated effectively in the *para*-position with high levels of conversion and yield, while, at the same time, utilising a minimum amount of catalyst and nitrating reagent. It has been established that the reaction can be conducted successfully in an autoclave at room temperature using air pressure of 200 psi and in the absence of solvent. The best catalyst for this reaction is zeolite Hβ with a silicon to aluminium ratio of 12.5, and the substrate to nitrating reagent

ratio should be 1:1.4 for the best results. The time required for 100% conversion of chlorobenzene to products was 14 hours.

Using these parameters as a basis for further experiments, the nitration of several other aromatic compounds was attempted using zeolite Hβ (3.0 g), substrate (33 mmol), liquid dinitrogen tetroxide (1.4 ml, 23 mmol), and 200 psi air. The reaction times used for each experiment and the results of each experiment are shown in Table 4.11.

Table 4.11. The Reaction Time, Conversion, Yield, and Isomer Distributions Formed During the Nitration of Different Aromatic Substrates.[a]

Substrate	**Time**	**Conversion[b]**	**Yield[b]**	**Isomer Distribution[b] (%)**		
	(h)	**(%)**	**(%)**	***ortho***	***meta***	***para***
Toluene	24	86	76	50	3	47
Benzene	22	100	97	-	-	-
Fluorobenzene	16	100	95	9	<1	91
Chlorobenzene	14	100	97	15	<1	84
Bromobenzene	14	97	90	19	<1	80

[a] All reactions were carried out with substrate (33 mmol), zeolite Hß (3.0 g), dinitrogen tetroxide (1.4 ml, 23 mmol), and air (200 psi) at 25 °C. [b] Calculated by quantitative GC.

The results show that all of the substrates tested gave good yields of nitration products, with modest increases in the amounts of *para*-isomer in comparison with traditional methods. The *para*-selectivity of the nitration reaction using the halogenobenzenes and toluene under these reaction conditions does not differ significantly from the *para*-selectivity seen using the method developed and

discussed in Chapter 3. However, the results when benzene was used as the substrate in this system are radically improved. In Chapter 3, nitration of benzene using zeolite Hβ, dinitrogen tetroxide, and oxygen with 1,2-dichloroethane solvent resulted in a 55% conversion with 50% yield. In contrast, use of benzene in the current system results in 100% conversion and 97% yield. The nitration of iodobenzene was attempted using this system, however, the results for the nitration of iodobenzene are not reported. The nitration of iodobenzene was attempted using the same protocol as described for all of the other aromatic compounds, however, in this case, the reaction proceeded for one minute, then exploded. The reason for the explosion was unclear, however, it is apparent that other experimental parameters will need to be employed if iodobenzene is to be nitrated using this system.

4.4 Stoichiometry and proposed mechanism of the aromatic nitration reaction using dinitrogen tetroxide

An attempt to understand the stoichiometry of the nitration reaction was made using chlorobenzene as the reaction substrate. It was of interest to identify the reaction stoichiometry, since it was not known whether the by-product of the reaction was water, nitric acid or a mixture of the two. Equation 4.1 (n = 0-6) is a general one that covers the various possibilities for the reaction.

$$24\ ArH + (12+2n)\ N_2O_4 + (6+n)\ O_2 = 24\ ArNO_2 + 4n\ HNO_3 + (12-2n)\ H_2O \quad (4.1)$$

A series of reactions involving different proportions of chlorobenzene to dinitrogen tetroxide was allowed to react to completion. The ratio of chlorobenzene to dinitrogen tetroxide was based on an average density value of 1.5 g/ml for dinitrogen tetroxide which was determined experimentally at temperatures ranging from –10 °C to –13 °C. The results are shown in Table 4.12.

Table 4.12. Amount of dinitrogen tetroxide used, reaction time, and HNO_3 recovered during stoichiometric study.[a]

N_2O_4 (ml)	N_2O_4 (mmol)	C_6H_5Cl : N_2O_4 Ratio	Time (h)	HNO_3 (mmol)
0.5	8.3	1:0.25	46	3.2
1.0	16.5	1:0.5	46	7.2
1.0	16.5	1:0.5	168	7.1
1.4	23.1	1:0.7	46	7.8
2.0	33.0	1:1	46	7.9

[a] All reactions were carried out with chlorobenzene (33 mmol), zeolite Hß (3.0 g), and air (200 psi) at 25 °C.

The results of leaving a mixture of 4 equivalents of chlorobenzene with 2 of N_2O_4 under air pressure for 4 days showed a yield of nitro product of only 73%. This suggested that 3 moles of ArH reacted with 2 moles of N_2O_4 to give 3 moles of nitro product.

Titration of the solution obtained by washing the reaction mixture with water revealed the presence of acid corresponding to 22% of the N_2O_4 used. We conclude that the most likely value of n in Equation 4.1 is 2, leading to the simplified stoichiometry of Equation 4.2.

$$3\ ArH + 2\ N_2O_4 + O_2 = 3\ ArNO_2 + HNO_3 + H_2O \qquad (4.2)$$

Figure 4.1 gives a tentative mechanism that is consistent with the apparent stoichiometry.

A similar overall result would be produced if NO_2 radicals were to abstract the first hydrogen atoms and the HNO_2 produced were then to react with oxygen to give $HOONO_2$. However, in that event it would not be easy to understand why the amount of nitration product obtained in the absence of oxygen is negligible. On the other hand, the reactivity of chlorobenzene, and the small differences in the catalytic activities of proton and sodium forms of the same zeolites do not seem to be in line with an acid-catalysed electrophilic substitution reaction under these conditions. We therefore suspect that the reaction is radical in nature. In addition, the relative reactivities of the substrates did not appear to be consistent with a normal electrophilic aromatic substitution mechanism. If the mechanism suggested in Figure 4.1 is the correct mechanism by which the nitration of aromatic compounds occurs, then nitric acid is one of the by-products of this reaction. According to our proposed mechanism, a NO_3 radical is formed prior to the formation of nitric acid. A hydroxyl radical would be the precursor to water.

With this knowledge, it may be possible to add another reagent, perhaps H_2O_2, to the reaction mixture, that would generate the hydroxyl radical directly, thus limiting the formation of nitric acid and resulting only in the production of the environmentally friendly compound, water.

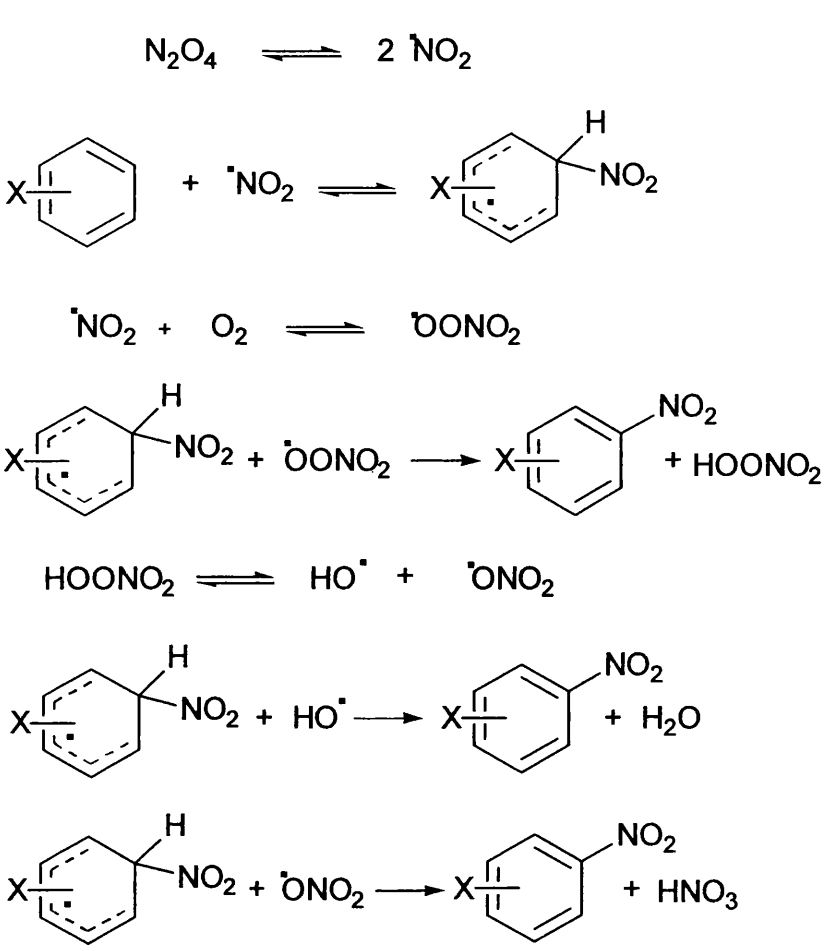

Figure 4.1. A speculative mechanism for the reaction. Any or all of the steps involving reaction of the substrate-NO_2 adduct with another radical could proceed by either of two mechanisms: (i) direct hydrogen atom abstraction; or (ii) electron abstraction to give a Wheland intermediate and an anion, followed by proton abstraction from the Wheland intermediate by the anion. Whether the zeolite would play an active part in catalysing any of the processes or merely assist through stabilisation of intermediates by adsorption is an open question.

4.5 Conclusions

Throughout the course of this project, it was important to improve upon current methods by which aromatic compounds could be nitrated. The two methods

of aromatic nitration described in Chapter 3 and in the current chapter result in the production of high yields of *para*-selectively nitrated aromatic compounds. At the same time, the methods designed and presented here are easy to use and, unlike most other nitration methods, produce only a limited amount of environmentally damaging compounds.

Although both of the methods developed during the course of this project offer significant advantages over traditional nitration methods, the current method in which an autoclave is used as the reactor during the course of the reaction offers additional advantages over the method described in chapter 3.

These advantages include a reduction in the reaction time from 48 hours to 14-24 hours, depending on the substrate used in the reaction, while still maintaining high yields and *para*-selectivity for the reaction products. At the same time, the amount of nitrating reagent used in the reaction has been drastically reduced without sacrificing the yield or regioselectivity of the reaction. In addition, when the smaller volume of dinitrogen tetroxide is used, the amount of substrate can be increased, along with an increase in the amount of catalyst, resulting in increased amounts of nitrated product obtained at the end of the reaction. Additionally, the reaction does not require solvent or the maintenance of low temperatures in order for it to proceed. And, this method was shown to increase the yield of nitrobenzene, a nitro product produced with the least amount of success with the method described in Chapter 3.

The advantages of the current method are not limited to the nitration protocol itself. There are also advantages associated with safety issues. For example, no acids

are used in the nitration reaction in either of the methods developed, and, in the current method, air, not oxygen, is used as the oxidation reagent.

Lastly, the results of the experiments in which the stoichiometry of the nitration reaction with chlorobenzene was evaluated have allowed for the proposal of a mechanism by which this reaction occurs.

Both of the methods developed and described in Chapters 3 and 4 suggest new methods by which aromatic nitration reactions can be accomplished easily and efficiently. The goals of this project, which were to develop methods by which aromatic compounds and halogenobenzenes could be nitrated have been accomplished through the study and development of these two methods in which catalysts were used to promote and facilitate the occurrence of the nitration reaction. There are still many aspects of these methods that need to be evaluated, however, the results obtained from experiments performed during the development of these methods demonstrate that improved procedures can be developed. Many aspects in the field of aromatic nitration remain to be explored. Further research into the mechanism of this reaction and how it can be optimised further, perhaps with the neutralisation of nitric acid, would make interesting subjects for future research projects.

4.6 References

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Papers

(1) Title: ***para*-Selective nitration of halogenobenzenes using a nitrogen dioxide- oxygen-zeolite system.**

K. Smith, S. Almeer and S. J. Black, *Chem. Commun.*, 2000, 1571.

(2) Title: **Regioselective mononitration of aromatic compounds by zeolite/dinitrogen tetroxide/air in a solvent –free system**
This work has been accepted in November 2001 (Ref. No. B108952H) for publication in *Chem. Commun.*

(3) A third manuscript dealing with this work is being prepared for submission for publication.